ERRATA

Pages

25 bottom line--essential, comma after triphenylene

36 1st equation = should be +

39 76.6 should be 66.6

57 line 3 dependences--dependences

67 bottom.equation $^3T + 2t \rightarrow 2p^* + T$

$^3T + 2t \rightarrow 2p + T$

72 $k_4 + k_5$ should be k_4 and k_5

76 $^3t \xrightarrow{k_9} p$

77 unimolecular quenching of ^3t

79 next to bottom line to--on

83 OH left out in symmetrical position to first OH in bottom formula

94 2,3-Diphenyl-butene-2 (top entry of table)

96 second line from bottom--observed goes to obscured

105 in the list below kinetic scheme--change 20 to 21; in second list, leave out 21

130 Ref. 3--change 3800 to 3880

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1967

PHOTOSENSITIZED CIS-TRANS ISOMERIZATION OF 2,3-DIPHENYLBUTENE-2

INVESTIGATION OF ANOMALOUS SENSITIZERS

FOR SUBSTITUTED STILBENE ISOMERIZATION

Thesis by

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Dedicated to Dr. Kenneth Eells, without whose sympathetic encouragement this work could not have been completed.

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To my husband, Don, whose genuine desire that I engage myself in this work, even during such times as it inconvenienced his own endeavors, I express warm admiration and appreciation.

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ABSTRACT

The behavior of the photosensitized cis-trans isomerization of 2,3-diphenylbutene-2 was studied as a function of sensitizer energy by previously established methods. In addition, certain sensitizers for which parameters other than energy transfer are operative in inducing isomerizations, were studied in more detail. Sensitization of various stilbenes and substituted stilbenes by triphenylene is discussed in terms of excited state complex formation with stilbene. Sensitization by quinones, halogen-containing aromatics and 1,2-diketones is discussed in terms of attack by photolytically produced free radicals, either by addition to and elimination from the double bond, or in the cases of 1,2-diphenylpropene and 2,3-diphenylbutene-2, by hydrogen abstraction from one of the methyl groups and reversible abstraction by the allylic radical to produce cis-trans isomerized substrate and the structurally isomerized products, 2,3-diphenylpropene and 2,3-diphenylbutene-1.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

P A R T 1

INTRODUCTION

The detailed nature of participation by sensitizers in photochemical processes is a subject which has been investigated only scantily, but has been debated warmly throughout the development of photochemistry. In the extreme types of photochemical reactions (assumed to be triplet, unless otherwise stated), the energy donor can "pump" its excitation energy actively into the acceptor, or passively be drained of this excitation energy by the acceptor. For the intermediate cases, varying degrees of mutual cooperation or antagonism may be encountered.

The limit of active participation by the sensitizer can, perhaps, be best exemplified by the diradical model of sensitized reactions strongly advocated by Schenck (1) to explain photochemical oxidations. According to this model there are two possible pathways for chemical reaction.

TYPE I

$$S + h\nu \longrightarrow \cdot S \cdot \qquad (1.1.1)$$

$$\cdot S \cdot + AH \longrightarrow SH \cdot + A \cdot \qquad \text{primary} \qquad (1.1.2)$$

$$A \cdot + O_2 \longrightarrow AOO \cdot \qquad (1.1.3)$$

$$AOO \cdot + AH \longrightarrow AOOH + A \cdot \qquad \text{propagation} \qquad (1.1.4)$$

$$AOO \cdot + SH \cdot \longrightarrow AOOH + S \qquad \text{termination} \qquad (1.1.5)$$

TYPE II

$$\cdot S \cdot + O_2 \longrightarrow \cdot SOO \cdot \qquad (1.2.1)$$

$$\cdot SOO \cdot + A \longrightarrow S + AO_2 \qquad (1.2.2)$$

Although this would appear to give a reasonable description of such reactions, it has been severely criticized by Foote and Wexler (2,3) who have given convincing evidence that singlet oxygen is the true photochemical intermediate.

$$S \longrightarrow {}^1S \qquad (1.3.1)$$

$${}^1S \longrightarrow {}^3S \qquad (1.3.2)$$

$${}^3S + {}^3O_2 \longrightarrow {}^1O_2 + S \qquad (1.3.3)$$

$${}^1O_2 + A \longrightarrow AO_2 \qquad (1.3.4)$$

For many other systems to which Schenck has generalized this mechanistic scheme, the necessity for such a complex system of intermediates becomes highly questionable. Hardham's (4) work on the photosensitized cyclo-addition of maleic anhydride to benzene (which will be mentioned in another connection later) and the work done by this group (5) on the dimerization of coumarin are two examples. Certainly the Schenck mechanism is not generally applicable to the cis-trans isomerization of stilbenes. The main objection is that the model involves such close coupling of sensitizer and substrate that in favorable cases one might expect the coupling to be permanent, thus forming a sensitizer-substrate compound. It is the notable absence of such compounds from the stilbenes, as well as from other systems, which has thrown the Schenck mechanism into general disfavor for explaining most simple photochemical transformations and decompositions. However, as will be seen, it may be necessary in some specialized cases, to adopt a scheme similar to the Schenck mechanism to explain the behavior of certain sensitizers.

The early interpretation of sensitized cis-trans isomerization of the stilbenes in terms of a simple energy transfer mechanism by Saltiel and Hammond (6) represents the prototype of ultimate sensitizer passivity. The sensitizer, according to this mechanism, undergoes only electronic configurational changes throughout the entire energy transfer step. After transfer has been completed, the sensitizer is left devoid even of more than a small amount of vibrational excitation. Evidence for such exhaustive removal of sensitizer energy is given by the fact that the characteristic triplet energy of the sensitizer in producing cis-trans isomerizations appears to be that of the 0-0 band.

A major reason for lack of detailed information on the step-by-step participation of the sensitizer in energy transfer can be attributed to the difficulty of finding effective direct techniques for monitoring the condition of the excited sensitizer-substrate unit. Almost all the techniques which have proved useful to date employ either measurement of differences in the bulk properties of sensitizer solutions in the presence and absence of added substrate, or measurement of properties characteristic of the solution after the reaction has been completed. Fortunately, a significant amount can be deduced about what must or might have occurred, even so.

Reactions induced by simple energy transfer are usually classified as such by default. There exists no distinguishing property other than a shortening of the sensitizer lifetime in the presence of an acceptor. In the case of stilbene isomerization, the photostationary ratio of isomers can be predicted from a knowledge of the stilbene triplet decay ratio and the flash photolytic quenching constants character-

istic of the various sensitizers. At the photostationary state, (7)

$$\frac{[t]}{[c]} = \frac{k_{T \rightarrow t}}{k_{T \rightarrow c}} \quad \frac{k_{q(cis)}}{k_{q(trans)}} \tag{1.4}$$

T represents either a single triplet intermediate of stilbene or an equilibrated mixture of two intermediates. The k_q's are first order quenching constants of triplet-triplet absorption of the excited sensitizer by stilbene. As for the other spectroscopic properties of the solution, they remain unchanged. The absorption spectra, either $S^0 \rightarrow S^1$, or $T^1 \rightarrow T^2$ are unaltered, and the emission (in the rare cases where phosphorescence in fluid solutions exists) may be quenched, but retains its spectral distribution. Clearly no permanent, or even temporary, chemical changes may have been made in the sensitizer. The effect produced by these non-interacting triplet sensitizers is characteristic only of their triplet energy. It would appear presently, that for a large number of sensitizers, the above description is adequate to explain cis-trans isomerization in numerous systems (8), including the stilbene systems, piperylene, ethyl maleate - ethyl fumarate and to some extent, diphenylcyclopropane. Furthermore, this description is not confined only to the isomerization reaction but is adequate to explain many other reactions also. Examples include the sensitized cyclo-addition of several acyclic and cyclic dienes (9), the addition of dienes to perhaloethylenes (10) and the sensitized decomposition of diazomethane (11).

The nature of triplet energy transfer differs qualitatively from the common mode of singlet energy transfer (12) in that it can occur only at short range, i.e., it is collision controlled. Transfer of singlet energy, by the Förster mechanism occurs between species whose

electronic systems are coupled by means of their transition dipole moments. The triplet interaction between two unlike molecules is thought to result from electronic exchange terms in the interaction energy (13). Overlap of the electronic wave functions is required for the exchange interaction. The wave functions for electrons centered on either the donor or the acceptor drop off exponentially with distance, so unless the separation between donor and acceptor is small there will be only a negligible interaction. Since we are dealing with overlap between two different electronic distributions, it would not seem at all surprising if the details of sensitizer and acceptor geometry were to exert some subtle influences on energy transfer efficiencies. Here, already, the sensitizer is being required to cooperate in a more active manner by orienting itself in a favorable configuration with respect to the acceptor.

Such effects have been elegantly demonstrated to exist by El Sayed (14), who used knowledge of donor absorption and acceptor emission polarizations to demonstrate that the maximum amount of energy transfer occurs between benzophenone and phenanthrene-d_{10} in the configuration where the molecular plane of the phenanthrene is parallel to the CO axis of benzophenone. This is also the configuration which permits the greatest overlap of electronic distributions of the corresponding triplet states.

The experimental investigation of such distance of approach and orientation parameters can take any one of numerous other varied directions. One of the first to be investigated in these laboratories was Jones' work (15,16) on sterically hindered ketones as *sensitizers for*

the stilbene isomerization. The results of photostationary state measurements and some flash photolytic quenching constants for various of these sensitizers with 2,3-diphenylbutene-2 and stilbene give some interesting, if not entirely clear-cut, evidence for a steric effect on the efficacy of energy transfer from the hindered carbonyl group. In both cases, the isopropyl compounds give anomalous results. Flash photolytic studies were made to determine whether the photostationary state deviations resulted from steric inhibition of energy transfer, or from sensitization or quenching of stilbene by the photoenols produced from such sensitizers by internal hydrogen atom abstraction (17). It appears that stilbene quenches the enolization, but does not effect the lifetime of these transients. The rate of enolization quenching is much greater with the trimethyl compound studied, than it is with the triisopropyl compound. It would therefore appear that deviations from the expected photostationary state can best be accounted for by steric hindrance to energy transfer. Quantum yields were not measured in order to determine whether absolute rates of transfer were affected for those sensitizers which gave normal photostationary states. However, the photostationary state measurement alone implies strongly their behavior as normal high energy sensitizers, since it gives the value associated with the natural decay ratio, or diffusion controlled transfer to both isomers. This work appears in Table 1.

Studies of intramolecular energy transfer in various systems of non-conjugated chromophores open up an entirely different area for investigation of subtle steric influences on energy transfer efficiencies. Lamola and Leermakers (18) have done work on systems of naphthalene joined

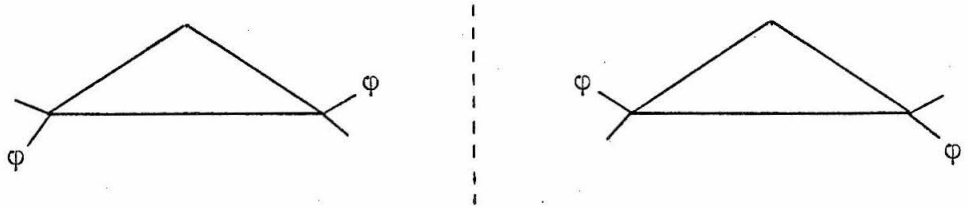
TABLE 1

Isomerization by Sterically Hindered Ketones

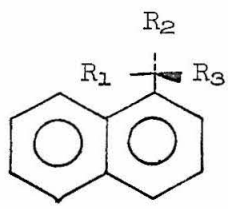
Substrate	Sensitizer	E_T (sensitizer)	$\frac{[cis]}{[trans]}$ expected	$\frac{[cis]}{[trans]}$ observed
Stilbene	2,3,5,6-Tetramethyl-4'-methoxybenzophenone (1)	70.2	1.47	1.45 ± .02
	2,4,6-Trimethyl-4'-methoxybenzophenone (2)	68.4	1.47	1.47 ± .03
	2,4,6-Triisopropyl-benzophenone (3)	68.7	1.47	1.92 ± .02
	2,4,6-Triisopropyl-4'-methoxybenzophenone (4)	69.9	1.47	1.93 ± .04
			$\frac{[trans]}{[cis]}$ expected	$\frac{[trans]}{[cis]}$ observed
2,3-diphenyl-butene-2	(1)		3.3	3.17
	(2)		3.3	3.27
	(3)		3.3	8.38
	2,4,6-Trimethylphenyl-2-naphthyl ketone	56.3	15.8	16.0
	Triphenylmethyl phenyl ketone	69.3	3.3	3.4

to benzophenone by methylene bridges of varying lengths. Schnepp (19) has done similar work with naphthalene joined to anthracene in the same manner. In both cases, efficient transfer of both singlet and triplet energy was noted from the chromophore of higher energy to that of lower energy. However, there was no simple relationship between transfer efficiency and length of the methylene bridge. This observation implies that the molecules are flexible enough to orient their chromophoric groups with respect to each other in a manner most conducive to short range energy transfer. The fact that in Lamola's compounds the efficiency of transfer was not the same for the three compounds indicates that this orientation may be fairly highly specific.

A highly productive area of research into these questions is being explored by Cole (20) in his work with asymmetric induction. The most successful experiments have been done with diphenylcyclopropane cis-trans isomerization. The trans isomer has two optically inequivalent forms. When cis-trans isomerization is



induced by sensitizers of the form



the following kinetic scheme has been found to be applicable.

$$(-)^3S + (-)A \xrightarrow{k_-} (-)S + (-)^3A \qquad (1.5.1)$$

$$(-)^3S + (+)A \xrightarrow{k_+} (-)S + (+)^3A \qquad (1.5.2)$$

$$(-)^3A \xrightarrow{k_{d-}} \underline{cis} \qquad (1.5.3)$$

$$(+)^3A \xrightarrow{k_{d+}} \underline{cis} \qquad (1.5.4)$$

Optical rotation is induced in such solutions to an extent which implies a difference of from 10-20% in the rate constants k_- and k_+. However, the interpretation of this work is still somewhat ambiguous as a result of complications introduced by direct absorption processes and side reactions.

Almost assuredly an increasing number of such cases of sensitizer steric-effects on energy transfer efficiency will be discovered as more sensitive measuring techniques are discovered.

Still further in the direction of active sensitizer involvement in the energy transfer process are the cases in which a distinct excited state complex is formed between donor and acceptor. Such a complex formation would be expected to result in a different decay ratio to final products from that resulting from simple energy transfer. Examples of the possible effects of complex formation will be given in the section on triphenylene sensitized stilbene isomerization. This difference could occur as a result of the difference in energy of the sensitizer-substrate complex from that of the free sensitizer, or from the more rigidly confined relative orientation of sensitizer and acceptor. It seems highly likely that both factors contribute to the overall product ratio.

A well documented case of sensitizer-acceptor complex formation acting as the intermediate step in a photochemical process is the maleic anhydride-benzene system studied by Hardham (21). Here the maleic anhy-

hydride-benzene complex is excited to its triplet state which then decays to a monoadduct. This adduct then thermally adds to another maleic anhydride to form the final product.

Further extensive work on the coumarin (22) system implies that for the direct isomerization in ethanol (which leads to the cis head-to-head dimer) the intermediate is a singlet excimer.

Some rather interesting experiments have been done by Sahyun (23) which imply resoundingly that complex formation is not of general importance in the stilbene system. The results which he has obtained using stilbene-sensitizer charge-transfer complexes both as sensitizers and triplet quenchers are presented below.

TABLE 2

Effect of Complex Formation, Sensitization Experiments

Complex	Light Source	Irradiation Time	Reaction Observed
t-Stilbene · Picric acid	Hg 4047, 4350	4 days	No reaction
t-Stilbene · Tetrocyano-ethylene (TCNE)	Na 5889	6 days	No reaction
c-Stilbene·TCNE	Na 5889	6 days	No reaction
c,t-Stilbene · 2,4,7-Trinitro-fluorenone	Hg 4047, 4350	2,3 days	Acts like low energy sensitizer

TABLE 3

Effect of Complex Formation, Quenching Experiments

Solution	Light Source	Irradiation Time	Reaction
c-Stilbene· TCNE	Hg 3660	6d	33% t
c-Stilbene	Hg 3660	6d	41% t
c-Stilbene· TCNE	Hg 3660	Photostationary state	40 ± 2% t
c-Stilbene	Hg 3660	Photostationary state	42 ± 1% t

All of the above reactions can be accounted for in terms of direct irradiation of the stilbenes. The difference in rate results from the fact that stilbene gets only 6% of the light in the presence of TCNE and 15% when irradiated separately. For the complexes looked at there is no evidence to support the supposition that the charge transfer complex can act as either a sensitizer or a quencher for stilbene isomerization. This work is of importance because the Saltiel kinetic mechanism is incapable of distinguishing between simple energy transfer and formation of a short lived molecular complex. Also, it has been hypothesized that some sensitizers which do not give normal photostationary states might use inefficient formation of a complex as a mode for wasting energy. Energy wastage will effect the photostationary state only if there is preferential complex formation from one of the isomers. However, this preferential formation is a well-known phenomenon (24).

The formation of a complex can effect quantum yield or photostationary state measurements by another mechanism as well. Up until

now interpretation of diene dimerizations and olefin isomerization has completely ignored contributions from excited singlet states. However recent work (25) has been done which indicates that there are some modes of energy dissipation to be considered from these states also. Piperylene and cyclohexadiene have been found to quench fluorescence of various aromatic hydrocarbons at a rate which sometimes approaches that of diffusion. This quenching occurs in spite of the fact that the diene singlets lie considerably higher than those of the aromatic sensitizers. In the cases studied, this process does not appear to lead to triplet products in appreciable yield, but does occasionally lead to new products. Related work done using stilbene as a quencher has given indeterminate results so far. This is because the quenching process is complicated by competitive absorption into stilbene itself.

While it is not entirely clear whether complex formation is germane to the stilbene problem as it presently stands, certainly there exists a considerable potential for unearthing sensitizers for which it needs to be taken into consideration.

The degree of interaction which leads to a reversible chemical change in the sensitizer has been discussed in connection with the Schenck mechanism. A large portion of this thesis will be devoted to what are apparently reversible chemical reactions between stilbene and sensitizer which culminate with isomerized stilbene as the product of primary interest.

As mentioned previously, the ultimate degree of sensitizer-acceptor interaction would entail addition or some other form of permanent chemical reaction with the sensitizer. Whereas this does occur in numer-

our systems which have been studied, it is a complication, albeit a possibly eluminating complication, in the description of cis-trans isomerizations. Therefore, in the following discussion it will be considered only to the extent to which irreversible chemical reactions serve as a monitor to the course of the isomerization.

There are several classes of sensitizers for the various stilbene systems for which simple energy transfer seems hardly adequate to explain the behavior of the system in reaching a photostationary state. These sensitizers include triphenylene, the quinones, the 1,2-diketones, and various halogen containing aromatic compounds. It is these sensitizers which gave rise to the original complicated structure of the Saltiel plots for stilbene, 1,2-diphenylpropene and 2,3-diphenylbutene-2. The plots, modified by Herckstroeter and Valentine by leaving out quinones and halogen containing compounds, for the former two systems are shown on the following pages. Herckstroeter's measurements of triplet quenching constants for a variety of sensitizers by stilbene show the expected monotonic decrease (26) of quenching rate with $E_{acceptor} - E_{donor}$ when simple ketones or aromatic hydrocarbons are used as sensitizers. The extent to which the rates drop off more slowly than expected can be attributed to the flexibility of the stilbene molecule, which allows it to twist to a non-spectroscopic state in accepting energy. Unfortunately, but probably significantly, it has not been possible to obtain reliable quenching constant data with sensitizers in the above listed classes of deviant sensitizers.

Since the photostationary states obtained in the presence of these sensitizers are so radically different from those seen in the presence of isoenergetic sensitizers, and there are no obvious major

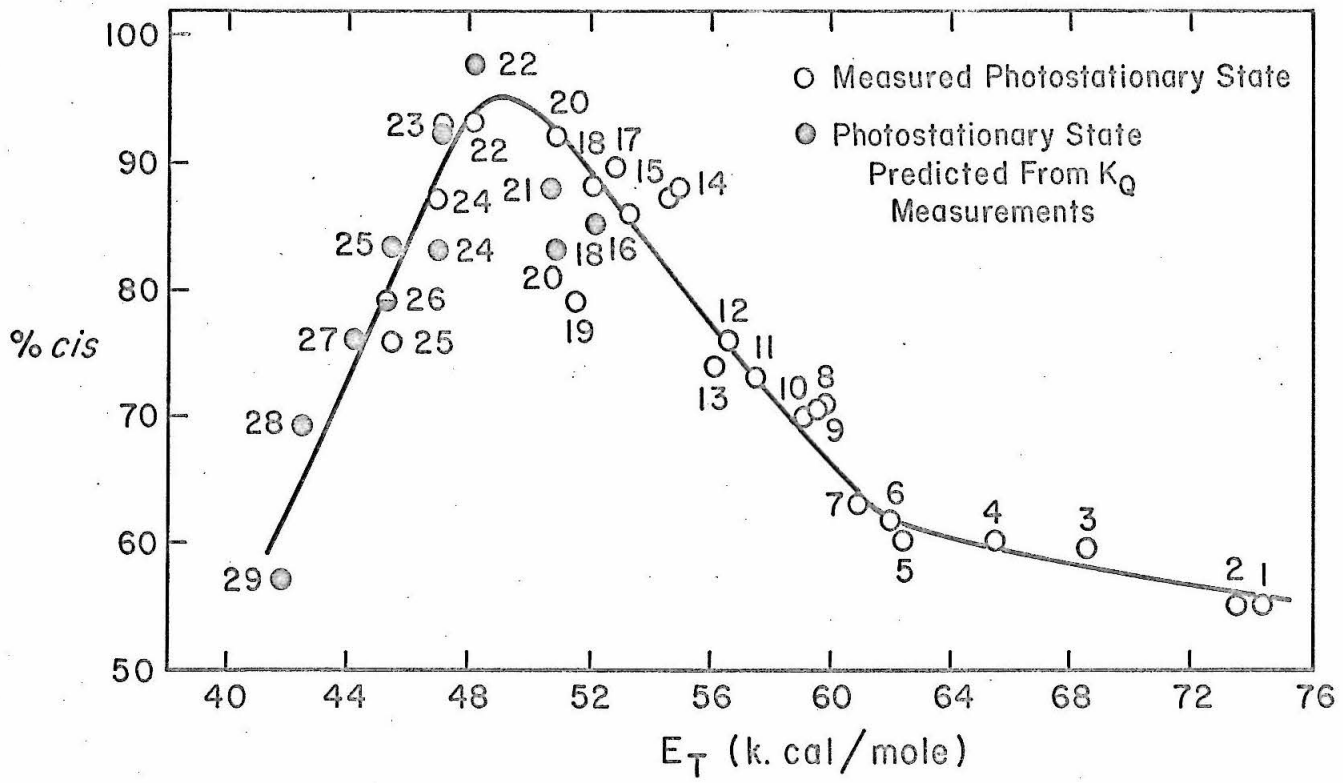


Figure I Corrected Plot for Photosensitized Isomerization of the Stilbenes

Figure 1

1. Cyclopropyl phenyl ketone
2. Acetophenone
3. Benzophenone
4. Thioxanthone
5. Anthraquinone
6. Flavone
7. Michler's ketone
8. 2-Napthyl phenyl ketone
9. 2-Naphthaldehyde
10. 2-Acetonaphthone
11. 1-Naphthyl phenyl ketone
12. Chrysene
13. 1-Naphthaldehyde
14. Biacetyl
15. Acetylpropionyl
16. Fluorenone
17. Fluoranthene
18. 1,2,5,6-Dibenzanthracene
19. Duroquinone
20. Benzil
21. 1,2,3,4-Dibenzanthracene
22. Pyrene
23. 1,2-Benzanthracene
24. Benzanthrone

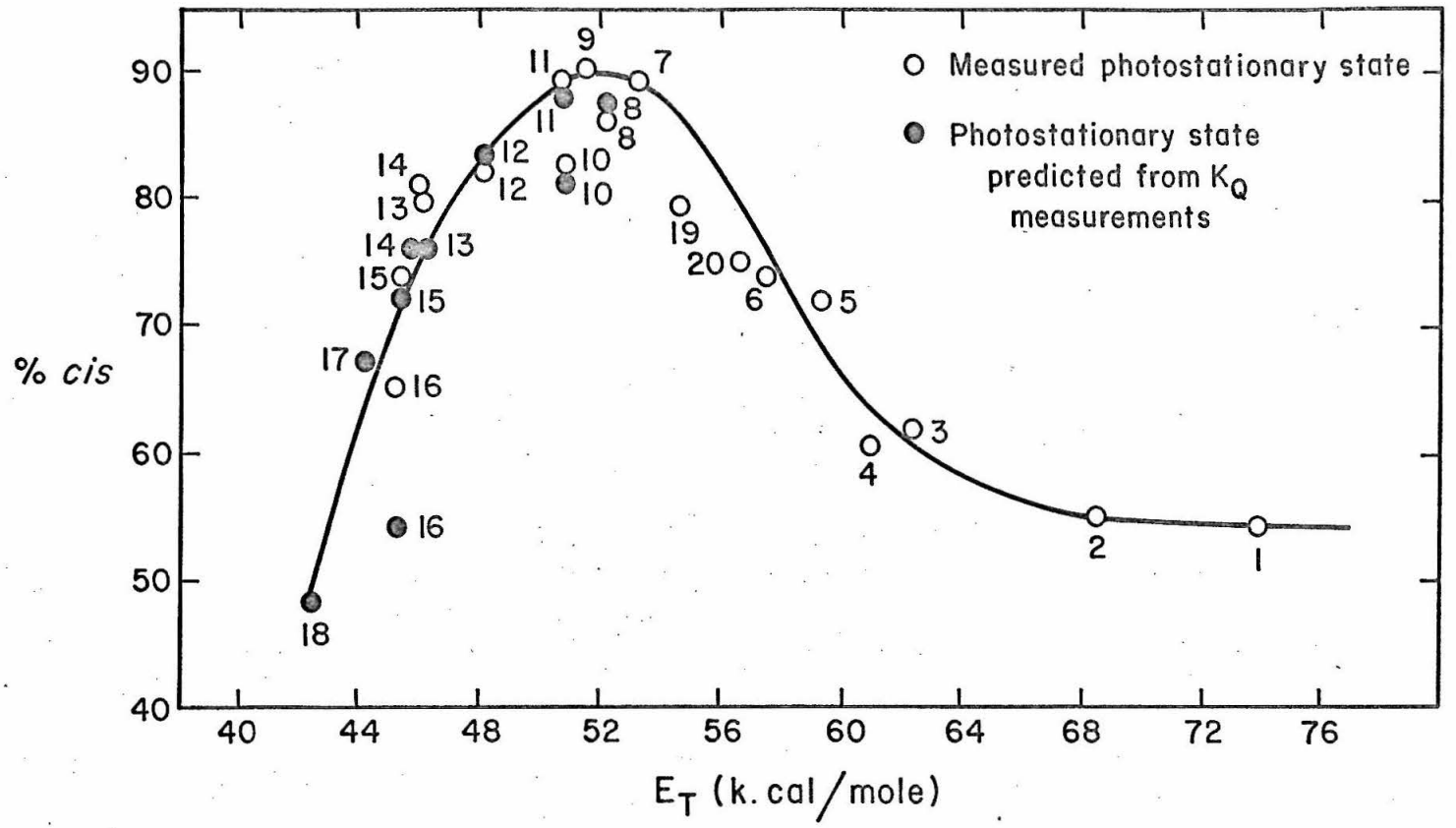


Figure 2 Photosensitized Isomerization of 1,2 Diphenylpropenes

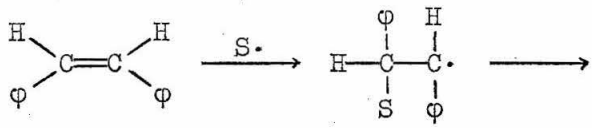
Figure 2

1. Acetophenone
2. Benzophenone
3. 9,10-Anthraquinone
4. Michler's ketone
5. 2-Acetonaphthone
6. 1-Naphthyl phenyl ketone
7. Fluorenone
8. 1,2,5,6-Dibenzanthracene
9. Duroquinone
10. Benzil
11. 1,2,3,4-Dibenzanthracene
12. Pyrene
13. 1,2-Benzanthracene
14. Benzanthrone
15. 3-Acetyl pyrene
16. Acridine
17. 9,10-Dimethyl-1,2-benzanthracene
18. Anthracene
19. Coronene
20. Chrysene

steric factors to be considered, it seems assured that processes are occurring which implicate active chemical participation of the sensitizer. The investigation of these processes will be directed primarly toward two likely sources. The first of these is complex formation, either in the ground or some excited state. Certain of the sensitizers of concern, namely the quinones, are known (27) to form ground state complexes with stilbene. However, in view of Sahyun's work this hardly seems to be of major importance.

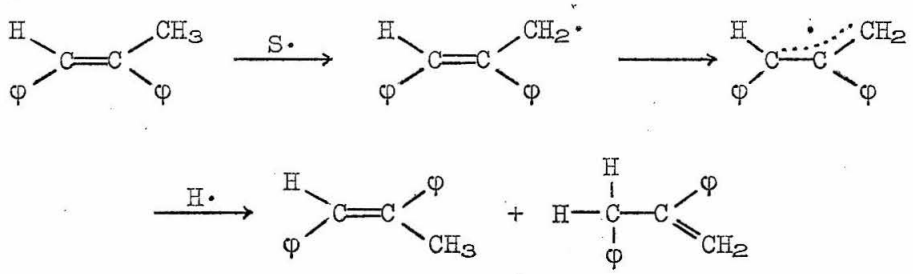
The other proposed explanation stems from the well documented fact that sensitizers in three of the four anomalous classes are capable of undergoing photochemical reactions which produce free radicals (28,29, 30,31).

Depending on the stilbene system under consideration, it is possible to produce cis-trans isomerization from free radicals by either one of two different mechanisms.



(1.7)

products, isomerized stilbenes



(1.8)

Although the allylic radical is traditionally considered to be incapable of free rotation, most of the reactions which have been studied are so fast as to preclude meaningful tests of this hypothesis (32).

Triphenylene presents a less chemically reactive case from the other three types of sensitizers and will therefore be discussed in a separate section.

From the preceding discussion it should be evident that the detailed description of any given photochemical process is much more complex than might preliminarily be hoped. It is necessary to inquire about the mode of sensitizer interaction with a given acceptor not just for the given type of chemical reaction, but for each sensitizer with each acceptor individually.

In the following discussion the recently investigated dimethylstilbene system will be discussed in terms of the reappraised mechanism for isomerization. Also it will be attempted to elucidate in more detail the nature of the interaction between stilbene and the triplet states of the above mentioned classes of sensitizers for which energy is an insufficient interaction parameter.

PART 2

SENSITIZED ISOMERIZATION OF 2,3-DIPHENYLBUTENE-2

The photosensitized isomerization of 2,3-diphenylbutene-2 has been studied using the methods devised by Saltiel to study stilbene and extended to the study of 1,2-diphenylpropene by Bradshaw (33). 2,3-Diphenylbutene-2 resembles 1,2-diphenylpropene more closely than stilbene in its photochemical properties. The major qualitative and quantitative differences between 2,3-diphenylbutene-2 and the two systems previously described can be accounted for in terms of differences in the spectroscopic properties of the various stilbenes.

A plot of trans/cis ratio at the stationary state established in the presence of various sensitizers against triplet energy is given in Figure 3. The raw data are presented in Table 4. All of the experimental points have been included. Those which deviate markedly from the curve will be discussed individually or in groups of similar type at various later points in the discussion.

In comparing Figures 1, 2 and 3 the most striking feature in the 2,3-diphenylbutene-2 plot is the inversion of ratios of the isomer concentrations from those found with stilbene and 1,2-diphenylpropene. The latter compounds give cis-rich photostationary states as contrasted to the trans-rich values for 2,3-diphenylbutene-2. Furthermore, the entire 2,3-diphenylbutene-2 plot is "blue shifted" from that of its homologs.

Both of these characteristics can be readily explained in terms of the singlet-singlet absorption spectra of the three compounds. Table 5 gives the pertinent spectroscopic data.

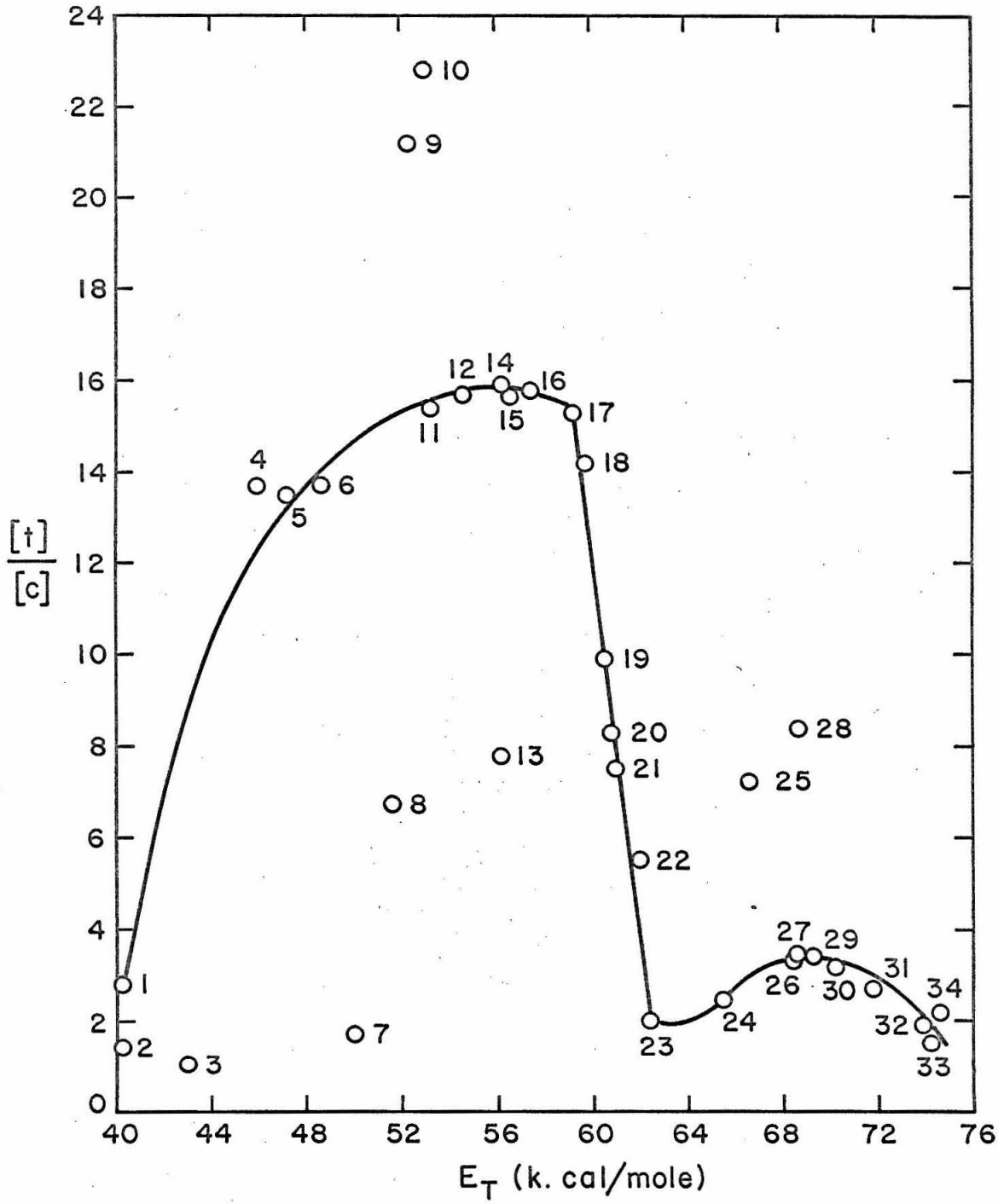


Figure 3 Photosensitized Isomerization of 2,3-Diphenylbutene-2

TABLE 4

Sensitized Isomerization Data[a]

	Sensitizer	E_T k. cals.	Filter System[b]	% trans	t/c
*1.	9,10-Dibromoanthracene	40.2	U	73.9 ± .5	2.83
*2.	Anthracene	40.2	U	58.4 ± .4	1.40
*3.	Eosin	43.0	U	50.6 ± .1	1.02
4.	Benzanthrane	46.0	U	93.2 ± .3	13.7
5.	1,2-Benzanthracene	47.2	U	93.1 ± .3	13.5
6.	Pyrene	48.7	P	93.2 ± .6	13.7
*7.	Benzoquinone	50.0	U	63.5	1.74
*8.	Duroquinone	51.6	U	87.0 ±1.6	6.69
9.	1,2,5,6-Dibenzanthracene	52.3	U	95.5 ± .5	21.2
10.	9-Fluorenone	53.0	U	95.8 ± .2	22.8
11.	Benzil	53.7	U	93.9 ± .2	15.4
12.	Coronene	54.6	U	94.0 ± .2	15.7
13.	α-Naphthaldehyde	56.2	U	88.4 ± .3	7.62
14.	Mesityl β-naphthyl ketone	56.3	U	94.1 ± .2	15.9
15.	Chrysene	56.6	U	94.0 ± .5	15.7
16.	α-Naphthyl phenyl ketone	57.5	U	94.0 ± .3	15.8
17.	β-Acetonaphthone	59.3	U	93.9 ± .4	15.3
18.	β-Naphthyl phenyl ketone	59.8	U	93.4 ± .2	14.2
19.	4-Acetylbiphenyl	60.6	U	90.8 ± .2	9.87
20.	β-Acetylfluorene	60.8	U	89.2 ± .3	82.6
21.	Michler's ketone	61.0	U	88.2 ± .1	7.47

TABLE 4--continued

	Sensitizer	E_T k. cals.	Filter System	% trans	t/c
22.	Flavone	62.0	U	85.1 ± .6	5.48
23.	Anthraquinone	62.4	U	66.8 ± .3	2.01
24.	Thioxanthone	65.5	U	71.5 ± .1	2.51
25.	Triphenylene	66.6	P	87.8 ± .4	7.20
26.	2,4,6-Trimethyl,4'-methoxy-benzophenone[c]	68.4	U	76.6 ± .3	3.27
27.	Benzophenone	68.5	U	77.4 ± .6	3.42
28.	2,4,6-Triisopropyl benzophenone[c]	68.7	U	89.3 ± .5	8.35
29.	Triphenylmethyl phenyl ketone[c]	69.3	U	~ 77.3	3.41
30.	p-Methoxyphenyl-2,3,5,6-tetramethylphenyl ketone	70.2	U	76.0 ± .4	3.17
31.	Benzaldehyde	71.9	U	72.9 ±1.4	2.69
32.	1,3,5-Triacetylbenzene	73.9	P	65.5 ± .3	1.90
33.	Xanthone	74.2	P	60.7	1.54
34.	Propiophenone[a]	74.6	U	68.5 ± .8	2.18

[a]The concentrations of both 2,3-diphenylbutene-2 and sensitizer were held at .05 M., except for those sensitizers which are insoluble to the extent of .05 M. and propiophenone which was used at .5 M. to absorb all the light. The insoluble sensitizers were used at saturation or near saturation values.

[b]P = pyrex sleeve
U = uranium glass sleeve

[c]These values were measured by Lee Jones.

*The starred compounds have been observed to give an initially cis rich photostationary state, then reverse to form a dramatically trans rich photostationary state. The 1,2-diketones triphenylene and pyrene do this to a lesser degree.

TABLE 5

Singlet Energies of Stilbene Systems

	Stilbene		1,2-Diphenylpropene		2,3-Diphenylbutene-2	
	cis	trans	cis	trans	cis	trans
$\lambda_{max.}$ of 1st absorption band (Å)	2800	2945	2670	2720	2520	2435

Not only are the absorption maxima blue shifted with increasing substitution at the ethylenic double bond but also the cis and trans singlet excitation energies approach each other and have crossed in the case of 2,3-diphenylbutene-2. The differences in the Saltiel plots for the three compounds follow from these data if one makes the assumption that the excitation energies of lowest triplets fall in the same order as those of the lowest excited singlets.

In this reversal lies a complementary piece of evidence refuting the original hypothesis that the structure of the Saltiel plots could be associated with vibrational structure in the "excitation spectrum" of the olefinic substrate having the lower triplet excitation energy. The trans spectra usually show well-defined vibrational structure, but the cis isomers generally have only structureless maxima. Since cis is the lower energy isomer for 2,3-diphenylbutene-2 the chemical spectrum would be expected to be structureless. However, the original structured Saltiel curve could have been drawn from the 2,3-diphenylbutene-2 data.

The "blue shift" is made to appear to be quite dramatic by the slowness with which the curve flattens out to approach the high energy

region such as was observed in contrast with the other stilbenes and various other substrates. Several attempts were made to find a suitable high energy sensitizer for the system. Tetraphenyl tin and tetraphenyl lead were used, in spite of the low extinction coefficients and low solubility, because light would be absorbed directly into the triplet state. Ethyl benzoate was used neat to compensate for its low extinction coefficient at 3130 Å because of the possibility that the lowest triplet might have higher excitation energy than aryl ketones and aldehydes. The results are summarized in Table 6.

TABLE 6

Possible High Energy Sensitizers

Sensitizer	E_T (k. cals.)	% trans at p.s.s.
Tetraphenyl tin	~ 83.6	90.4 ± .4
Tetraphenyl lead	83.6	92.3 ± .2
Ethyl benzoate	~ 80	92.2 ± .5

These values are close to the value 90.8 ± .7% trans obtained by irradiating 0.05 M. 2,3-diphenylbutene-2 in benzene with 3130 light. Unfortunately the latter result may not represent a photostationary state established by energy transfer from benzene triplets since the extinction coefficient is low and the result may have been influenced by the presence of low energy impurities. The metal compounds were badly decomposed and darkened by the light, presumably indicating formation of phenyl radicals and free metal. The subsequent reactions from the decomposition

probably determined the photostationary value. The ethyl benzoate may have contained impurities.

The constancy of the photostationary states from high energy sensitizers is attributed to the onset of sufficient energy in the sensitizer to effect diffusion controlled energy transfer to both isomers. Hence, the photostationary state is governed only by the natural decay ratio of the excited state intermediates. This high energy photostationary state uniformity has been questioned by Valentine (35), who prefers the thesis that at close approach, geometric factors affect the probability of energy transfer. Under these conditions no limiting value could be anticipated.

However, the work done by Whitten (36) on the radiochemical isomerization of stilbenes implies that direct γ irradiation of the stilbenes in benzene solution produces the same cis/trans ratio as would be anticipated from benzene, or some other high energy sensitization process.

TABLE 7

Ratiostationary States for Stilbene Systems

Substrate	Radiostationary State in Benzene	Average High Energy Photostationary State
cis, trans-Stilbene	58.8% cis	59.4% cis
cis, trans-1,2-Diphenylpropene	54.7% cis	54.8% cis
trans-2,3-Diphenylbutene-2	56.3% trans	60.0% trans
trans-Piperylene	57.5% trans	56.5% trans

The frequency with which values within experimental error of the high energy average are obtained would seem to imply strongly that a limiting value has indeed been reached. Now that it is clear that for many sensitizers isomerization can be initiated by factors beyond simple energy transfer, it seems more reasonable to attribute deviations from the high energy limit to low level competition from chemical mechanisms of isomerization.

Unfortunately, nothing is known directly about the 2,3-diphenylbutene-2 triplet states. 2,3-Diphenylbutene-2, like the other stilbenes, does not phosphoresce. An attempt was made to obtain the heavy atom-perturbed absorption spectrum. A solution of 1 M. trans-2,3-diphenylbutene-2 in ethyl iodide showed neither peaks nor long wavelength tailing. Actually the result is not surprising in view of the extreme weakness of 1,2-diphenylpropene absorption in ethyl iodide. With increasing substitution the stilbene singlet spectra show decreasing absorption intensities and increased broadening of the peaks.

More specific information can be gained about the triplet energies from the plot in Figure 3 itself. It is possible that the dip in the curve in the region of anthraquinone and thioxanthone is real. Certainly the inflection point followed by the sudden sharp rise in trans concentration indicating high efficiency of energy transfer to cis relative to trans is real. Therefore it seems imminently reasonable to assign the energy of the trans triplet to be ~ 65 to 66 k. cals. The broad maximum is very likely due to a competition between efficient transfer to cis and non-vertical transfer to both isomers. Thus the cis triplet probably lies at ~ 55 k. cals. or about 3 k. cals. below the point where

relative efficiency of transfer to cis ceases to increase rapidly in efficiency. At this 3 k. cal. point diffusion controlled energy transfer begins to falter for many compounds (37).

The outstanding difference between stilbene and 1,2-diphenylpropene photochemical behavior is experimentally manifested by the concentration effects produced by low energy sensitizers or quenchers and the effects of temperature on the photostationary state. These effects were explained by postulating a long-lived triplet intermediate for stilbene, but not for 1,2-diphenylpropene. The appropriate steps in the kinetic description are the following:

Stilbene:

$$ {}^3S + t \underset{k_{qS}}{\overset{k_{qt}}{\longleftrightarrow}} S + {}^3t \qquad (2.1.1) $$

$$ {}^3t \underset{k_{-dt}}{\overset{k_{dt}}{\longleftrightarrow}} p \qquad \text{fast equilibrium} \qquad (2.1.2) $$

$$ {}^3t + Q \underset{k_q}{\longleftrightarrow} {}^3Q + t \qquad (2.1.3) $$

$$ {}^3S + c \xrightarrow{k_{qc}} S + {}^3c \qquad (2.1.4) $$

$$ {}^3c \xrightarrow{k_{dc}} p \qquad \text{fast and irreversible} \qquad (2.1.5) $$

Reversible energy transfer was considered to be feasible only in those cases where the sensitizer is approximately isoenergetic with the trans triplet. The corresponding process for cis triplets was excluded because the presence of any quencher increases the concentration of trans at the photostationary state. For 1,2-diphenylpropene the scheme is

somewhat more compact to concur with the absence of temperature and concentration effects.

$$^3S + t \xrightarrow{k_{qt}} S + {}^3t \qquad (2.2.1)$$

$$^3t \xrightarrow{k_{dt}} p \qquad \text{fast, irreversible} \qquad (2.2.2)$$

$$^3S + c \xrightarrow{k_{qc}} {}^3c \qquad (2.2.3)$$

$$^3c \xrightarrow{k_{dc}} p \qquad \text{fast, irreversible} \qquad (2.2.4)$$

It is in the above mechanistic feature that 2,3-diphenylbutene-2 resembles 1,2-diphenylpropene rather than stilbene. There is no effect observed on the 2,3-diphenylbutene-2 photostationary states if the concentration of low energy sensitizers is varied or if a low energy quencher such as azulene is added to the solutions. The results obtained with added azulene and varying concentrations of certain sensitizers are reported in Tables 8 and 9.

Whereas the azulene effect would still seem to carry its classical interpretation as to the absence of a long-lived triplet of either isomer, the interpretation of sensitizer concentration effects must be slightly modified. The concept of reversible energy transfer was propounded under the Saltiel hypothesis that the lowest energy maximum in his plot represented the true 0-0 band for trans-stilbene. He made the additional assumption that isoenergetic energy transfer was diffusion controlled. Certainly it is energetically feasible for sensitizers with low triplet energies to quench stilbene triplets efficiently. However quenching of the sensitizer by the stilbene originally is quite slow,

TABLE 8

Azulene Effect

Sensitizer	Azulene Concentration	Photostationary State % trans
α-Naphthyl phenyl ketone	0.000 M.	94.8 ± .6
	0.005 M.	94.0 ± .3
	0.010 M.	94.8 ± .1
Thioxanthone	0.000 M.	72.2 ± .6
	0.005 M.	71.5 ± .6
	0.010 M.	71.5 ± .1
β-Acetonaphthone†	0.000 M.	93.3 ± .4
	0.005 M.	94.1 ± .5
	0.010 M.	95.7 ± .3

†There is good reason to suspect that these solutions had not quite reached photo stationary state.

TABLE 9

Sensitizer Concentration Effects

Sensitizer	E_T (k. cals.)	Sensitizer Concentration (moles/ℓ.)	Photostationary State (% trans)
9,10-Dibromoanthracene	40.2	0.01	74.9 ± .3[a]
		0.025	74.3 ± .1
		0.05	73.9 ± .2
		satd.	not at p.s.s.
Pyrene	48.7	0.01	93.1 ± .2
		0.025	93.6 ± .4
		0.05	93.2 ± .6
		0.10	93.3 ± .4
Benzil	53.7	0.01	93.8 ± .2
		0.025	94.0 ± .3
		0.05	93.9 ± .2
		0.10	94.3 ± .2
β-Acetonapthone	59.3	0.01	94.0 ± .1
		0.025	93.8 ± .4
		0.05	93.9 ± .5
		0.10	93.4 ± .3
Benzophenone	68.5	0.01	77.7 ± .7
		0.025	76.6 ± .3
		0.05	77.4 ± .6
		0.10	76.9 ± .4

[a]It is highly questionable whether these values represent a true photostationary state since competition with chemical processes either slows attainment thereof or destroys the stationary balance.

as evidenced by low quantum yields for isomerization and verified by Herckstroeter's slow quenching rates.

While the sensitizer concentration effect may in fact be entirely attributable to quenching of the trans-stilbene triplet, results which will be discussed later implicate the possibility of some form of chemical quenching particularly in the case of such sensitizers as acridine, benzanthrone and duroquinone.

It is evident from Figure 3 that the single maximum curve drawn through the experimental points represents the true deportment of the system only very incompletely. The remainder of this thesis will be devoted to examination of the numerous classes of deviant sensitizers, the quinones, the halogen-containing low energy sensitizers, the 1,2-diketones and triphenylene, in hope of clarifying the mechanism or mechanisms by which these sensitizers produce their observed or apparent photostationary isomer ratios.

PART 3

TRIPHENYLENE SENSITIZED ISOMERIZATION OF THE STILBENES

Background for the Study

Triphenylene is doubtless the least understood of all the sensitizers which have commonly been used by the Hammond group. Its triplet energy has been well confirmed (38,39,40) to be 66.6 k cals. per mole. Lamola determined its intersystem crossing yield to be 95%. Since it is not known to have any photochemistry of its own and should, to all external appearances, be inert towards all the compounds normally used as substrates, it should be a nearly ideal high energy sensitizer. However its individualistic approach to the sensitization of numerous reactions defies a simple explanation in terms of energy transfer.

Isomerization of the stilbenes as sensitized by triphenylene is complicated by the fact that competitive absorption occurs between the stilbenes and triphenylene. Therefore an accounting must be made of the amount of isomerization occurring by means of direct intersystem crossing of stilbene and that occurring through sensitization. The stationary state reached by the two concomitant processes can be deduced by setting the rate of production of cis from trans equal to that of production of trans from cis

$$t \rightarrow c = \alpha \varphi_{ic}\, \underline{trans}\, \frac{z}{1+z} + \gamma \frac{k_{qt}\,[\underline{trans}]}{k_{qt}\,[\underline{trans}] = k_{qc}\,[\underline{cis}]} \varphi_{ic}\ \text{sens.}\ \frac{z}{1+z} \qquad (3.1)$$

$$c \rightarrow t = \beta \varphi_{ic}\, \underline{cis}\, \frac{1}{1+z} \qquad \gamma \frac{k_{qc}\,[\underline{cis}]}{k_{qt}\,[\underline{trans}] + k_{qc}\,[\underline{cis}]} \varphi_{ic}\ \text{sens.}\ \frac{1}{1+z} \qquad (3.2)$$

where z = natural decay ratio of the stilbene intermediate

$$= \frac{[\underline{cis}]}{[\underline{trans}]} \quad \text{at p.s.s. from a high energy sensitizer with no direct excitation}$$

$$\alpha = \frac{\epsilon_{\underline{trans}}\,[\underline{trans}]}{\epsilon_{\underline{trans}}\,[\underline{trans}] + \epsilon_{\underline{cis}}\,[\underline{cis}] + \epsilon_{sens.}\,[sens.]}$$

$$\beta = \frac{\epsilon_{\underline{cis}}\,[\underline{cis}]}{\epsilon_{\underline{trans}}\,[\underline{trans}] + \epsilon_{\underline{cis}}\,[\underline{cis}] + \epsilon_{sens.}\,[sens.]}$$

$$\gamma = \frac{\epsilon_{sens.}\,[sens.]}{\epsilon_{\underline{trans}}\,[\underline{trans}] + \epsilon_{\underline{cis}}\,[\underline{cis}] + \epsilon_{sens.}\,[sens.]}$$

Substitute:

$$\varphi_{ic\ sens.} = .95$$

$$\varphi_{ic\ \underline{trans}} \simeq \varphi_{ic\ \underline{cis}} \simeq 1$$ (This approximation slightly over-emphasizes the contribution from the direct process)

Also, since triphenylene is a high energy sensitizer with respect to the stilbene systems, one may assume that

$$\frac{k_{qc}}{k_{qt}} = 1$$

Solving the equation obtained by setting the rates equal gives:

$$[\underline{trans}] = \frac{1}{z}\,\frac{c^2\,\epsilon_{\underline{cis}} + c\,\epsilon_{sens.}\,[sens.]}{c\,\frac{\epsilon_{cis}}{z} + \epsilon_{\underline{trans}} + [sens.]\left[\frac{\epsilon_{sens.}}{z} + \epsilon_{sens.}\right]}, \qquad (3.3)$$

where c is the total stilbene concentration.

Using the above formula for the concentration of trans and the following values for the concentrations, extinction coefficients and decay ratios, the theoretical photostationary data can be calculated.

Stilbene:
$$z = 1.6$$
$$\epsilon_{cis} = 4480\ \ell./\text{mole cm.}$$
$$\epsilon_{trans} = 24{,}000$$
$$c = [\text{sens.}] = .05\ \text{M.}$$
$$\epsilon_{sens.} = 910$$

1,2-Diphenylpropene:
$$z = 1.2$$
$$\epsilon_{cis} = 2140$$
$$\epsilon_{trans} = 4400$$
$$c = [\text{sens.}] = .05\ \text{M.}$$

2,3-Diphenylbutene-2:
$$z = .667$$
$$\epsilon_{cis} = 11 \quad \text{(in methanol)}$$
$$\epsilon_{trans} = 7.4 \quad \text{(in methanol)} \qquad (41)$$
$$c = [\text{sens.}] = .05\ \text{M.}$$

Table 10 compares these calculated values with the experimental data.

TABLE 10

Isomerization Sensitized by Triphenylene

Substrate	p.s.s. (calc.)	p.s.s. (curve)	p.s.s. (obs.)
2,3-Diphenylbutene-2	1.5 (t/c)	1.5	7.0
1,2-Diphenylpropene	2.1 (c/t)	1.4	0.67
Stilbene	7.3 (c/t)	1.6	0.86

It is clear that there is a large discrepancy between the observed photostationary states and those which are predicted by the plot (assuming the absence of direct isomerization) but that this discrepancy is made even larger, rather than corrected by accounting for the direct isomerization. If competitive absorption were always the most important perturbation, including the effect of direct irradiation should always shift the photostationary state in the direction of the isomer having the smaller extinction coefficient.

In the case of 2,3-diphenylbutene-2, the qualitative effect is in this expected direction, but is considerably larger than could be accommodated by the isomer extinction coefficient ratio. For 1,2-diphenylpropene and stilbene, however, inclusion of direct isomerization correction dramatizes rather than diminishes the deviation from the predicted 76.6 k. cal. photostationary state. This failure of the correction for direct isomerization to normalize the triphenylene data is emphasized even more impressively by observing the dependence of the photostationary state on the concentrations of sensitizer and substrate shown in Figures 4 and 5 for 1,2-diphenylpropene and 2,3-diphenylbutene-2.

Clearly for 1,2-diphenylpropene the expected increase of cis with increasing total stilbene concentration is completely obviated by an effect which favors the production of the trans isomer. This same observation is borne out again in the triphenylene concentration dependence. Increasing the triphenylene concentration is equivalent to decreasing the stilbene concentration since both decrease the fraction of the total process controlled by direct absorption of stilbene. Increasing the triphenylene concentration should therefore result in de-

creasing production of cis. However, just the opposite is observed to be the case.

For 2,3-diphenylbutene-2 the concentration effects are much more tenuous. While the qualitative direction of the variations is consistent with the thesis of competing direct and sensitized processes, the quantitative value of the photostationary states remains in question. Even at the lowest stilbene concentrations employed, the predicted curve value of 60% trans is not even closely approached.

Related anomalies have occurred when triphenylene was used as a sensitizer for other systems, such as the addition of maleic anhydride to benzene. In this case triphenylene acts like a sensitizer with less than 66 k.cals. of energy. Conversely triphenylene acts more efficiently than might be expected in the sensitized decomposition of certain azo compounds (42).

Possible Explanations and Qualifying Experiments

There are two ready trial explanations of these phenomena. One of these can be derived from the spectroscopic properties of the triphenylene triplet. Most of the aromatic hydrocarbons which have been used as sensitizers have their band of maximum phosphorescence intensity concentrated at or near the 0-0 (maximum energy) band. However, triphenylene has an exceedingly weak 0-0 band and the position of maximum intensity does not occur until 62.0 k. cals.

Making the not evidently unreasonable assumption that a small transition moment for the 0-0 radiative transition might be concurrently associated with a relatively low probability for non-radiative energy

loss in energy transfer, it seems possible that triphenylene might be unable to transfer its full complement of excitation energy, or at least not with high efficiency.

This principle can not be applied in its simplest form, however, because to explain the observed photostationary states, one would require that the minima be retained in the Saltiel plots. Even then, the triplet energy of triphenylene would have to be assigned to be ~ 56 k.cals. Neither of these conditions is acceptable. A further drawback to the principle of enhanced relative probability for energy transfer from allowed bands is the behavior of a geometrically and spectroscopically related aromatic hydrocarbon, coronene. Table 11 shows the types of photostationary states obtained from this compound, which has its 0-0 band at 55.5 k. cals. (43), but the energy of maximum intensity of which is at 50.8 k. cals.

TABLE 11

Photostationary States Reached in the Presence of Coronene as Sensitizer

Substrate	Filter	p.s.s. Experimental	p.s.s. Pred. by Plot (Herckstroeter Mod.)
t-2,3-Diphenylbutene-2	U	94.1 ± .2% t	94.4%
c-1,2-Diphenylpropene	U	79.1 ± .5% c	77.8%

These values do not take into account any variation in sensitizer concentration, as coronene is only sparingly soluble and was used at saturation concentration.

However, if one introduces not simply the postulate of reduced probability of energy transfer, but includes the additional stipulation that with such sensitizers as triphenylene and coronene some highly restrictive relative orientation requirements for donor and acceptor be satisfied, the original proposal regains vitality. A mechanism to describe these data will be considered further in the discussion section.

Another highly tractable proposal is the existence of some sort of complex intermediate. As has been previously mentioned in the introduction, the presence of either a ground or an excited state complex could effect the photostationary state.

Adherence of the triphenylene-stilbene systems to Beer's Law would appear to rule out the possibility of a ground state complex. The data obtained with 1,2-diphenylpropene as substrate are presented in Table 12.

TABLE 12

Beer's Law Applicability to 1,2-Diphenylpropene-Triphenylene System

λ(Å)	Δ cis	Δ trans (Δ's are in o.d. units)
3500	0.01	0.01
3400	0.00	0.00
3300	0.02	0.01
3200	0.01	0.01
3100	0.02	0.03
3000	0.02	0.09 (difference of two large nos.)

Δ cis = $\ell n \frac{I_o}{I}$ of [10^{-4}M. cis-1,2-diphenylpropene + 10^{-4}M. triphenylene]

$- \ell n \frac{I_o}{I}$ of [10^{-4}M. cis-1,2-diphenylpropene] $- \ell n \frac{I_o}{I}$ of [10^{-4}M. tri.]

Δ trans is analogous to Δ cis

There appeared to be no new absorptions from any new species between 3500 and 4000 Å in solutions that were 10^{-4} M. in both 1,2-diphenylpropene and triphenylene.

The most direct method for detecting an excited state complex would be by an emission spectrum. Excimers (excited dimers) of many aromatic compounds show characteristic fluorescence spectra (44). Solutions 10^{-3} M. in both triphenylene and trans-stilbene or trans-1,2-diphenylpropene or 10^{-2} M. in stilbene and 10^{-3} M. in triphenylene showed no anomalous emission, either fluorescence or phosphorescence, at both room temperature and liquid nitrogen temperature in benzene solution or MCIP glass.

However, phosphorescence from excimers or emission from excited state complexes of unlike compounds is not commonly observed for these types of systems, although it has been reported in complexes of trinitrobenzene with various aromatic hydrocarbons (45). Absence of emission, though in no way helpful, does not in any way guarantee the absence of an excited state complex in these systems any more than a low phosphorescence quantum yield guarantees a low intersystem crossing efficiency.

With the failure of the direct method to produce helpful results, more indirect methods for ascertaining the presence or absence of a new excited species were attempted. If the reactive intermediate is an excited state complex, a dependence of the photostationary state on the concentrations of the reactants and the temperature of the solution might reasonably be expected. The concentration dependences previously reported in Figures 4 and 5 could be interpreted in terms of a complex mechanism. Temperature dependence data for triphenylene and 1,2-diphenylpropene are shown in Table 13.

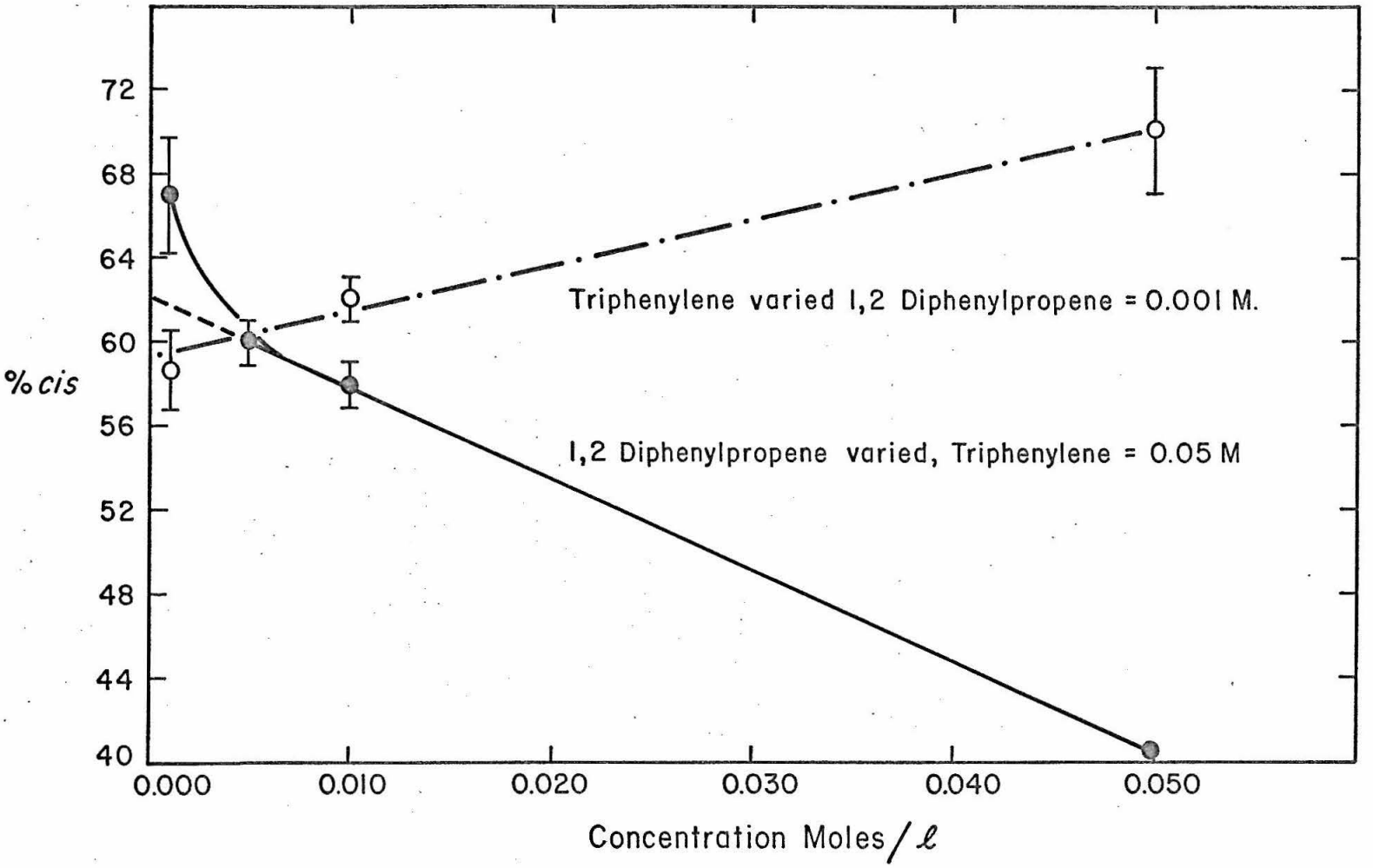

72
68
64
60
56
52
48
44
40
% cis
0.000
0.010
0.020
0.030
0.040
0.050
Concentration Moles/ℓ
Triphenylene varied 1,2 Diphenylpropene = 0.001 M.
1,2 Diphenylpropene varied, Triphenylene = 0.05 M

Figure 4

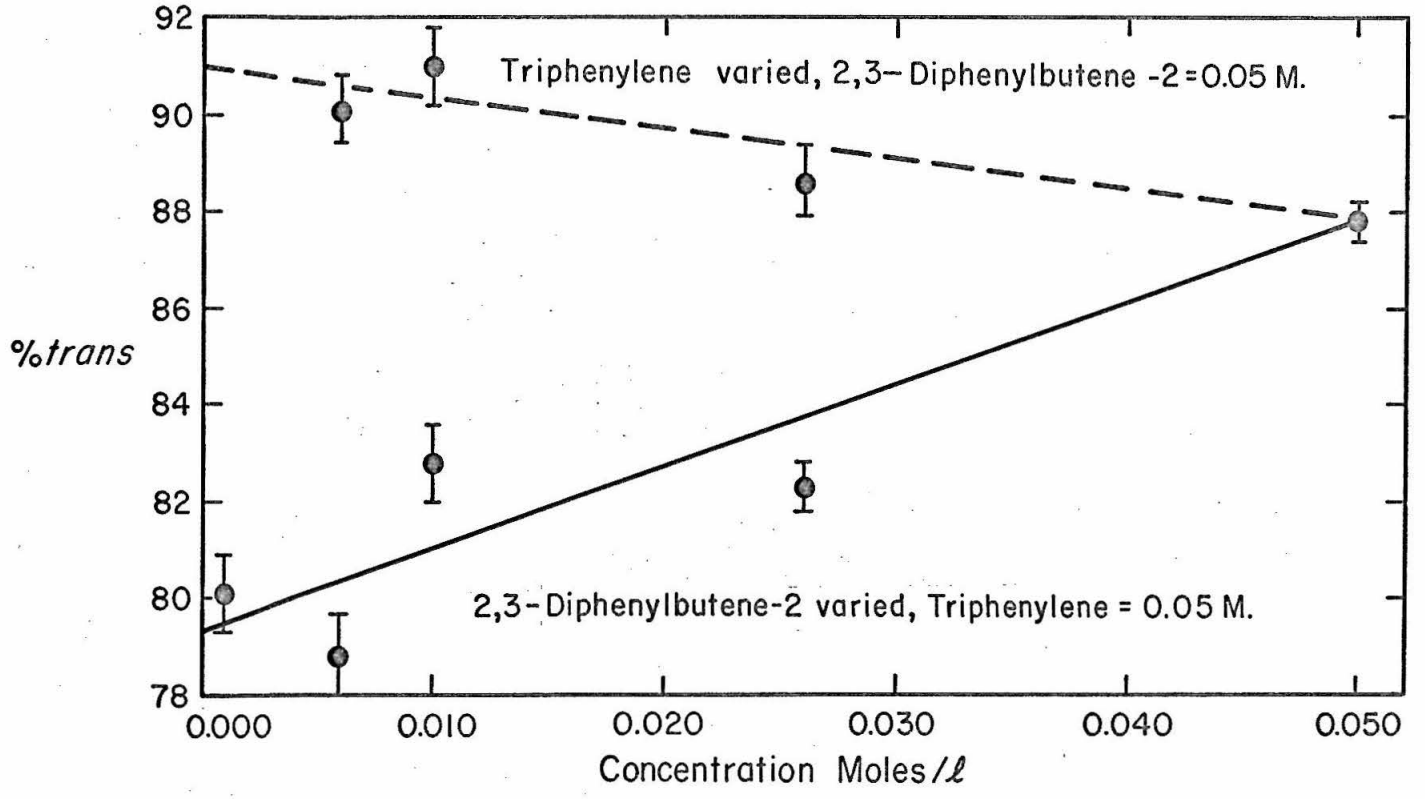

92
90
88
86
84
82
80
78
%trans
Triphenylene varied, 2,3-Diphenylbutene -2=0.05 M.
2,3-Diphenylbutene-2 varied, Triphenylene = 0.05 M.
0.000
0.010
0.020
0.030
0.040
0.050
Concentration Moles/ℓ

Figure 5

TABLE 13

Temperature Dependence of Triphenylene Sensitized
1,2-Diphenylpropene Isomerization

	1,2-Diphenyl-propene	Triphenylene	Temp.	% cis	
100% cis	0.001 M.	.05 M.	25° C.	68.3	68.0
100% trans	"			63.3	66.3
avg.	"			66.0 ± 3.5	67.1 ± 2.7
cis	0.01 M.		25° C	58.2	
trans	"			57.9	
avg.	"			58.0 ± 1.1	
cis	0.05 M.		25° C	40.1	
trans	"			42.6	
avg.	"			40.4 ± .47	
cis	0.001 M		40° C	67.6	
trans	"			67.1	
avg.	"			67.3 ± .8	
cis	0.01 M.		40° C	59.5	
trans	"			59.8	
avg.	"			59.6 ± .9	
cis	0.05 M.		40° C	43.3	
trans	"			43.5	
avg.	"			43.4 ± .6	
cis	0.001 M.		55° C	63.6	
trans	"			65.6	
avg.	"			64.4 ± 1.9	
cis	0.01 M.		55° C	63.5	
trans	"			59.5	
avg.	"			61.4 ± 2.9	
cis	0.05 M.		55° C	43.5	
trans	"			46.3	
avg.	"	.05 M.		44.9 ± 1.6	

There appears to be no temperature effect within experimental error. These data would imply that there is no heat of formation for the complex and that it decays so rapidly into products that there is not time for equilibration between the complex and the dissociated excited state and ground state moeities.

If the mechanism for the sensitization process is to be understood, in detail, it is important to ascertain whether sensitization occurs from a singlet or triplet state of triphenylene, or the stilbene itself, since the direct irradiation of stilbene can not be avoided. Two types of experiments have been done with hope of determining the multiplicity of the excited intermediate, but the results of both were to a large extent ambiguous.

The first of these experiments were measurements of fluorescence quenching with triphenylene and stilbene or 2,3-diphenylbutene-2. In the case of 2,3-diphenylbutene-2, solutions were made up containing approximately 10^{-3} M. triphenylene and .5 or .025 M. trans 2,3-diphenylbutene-2. In each case there was no more quenching than could be attributed to competitive absorption from the stilbene. In the stilbene experiments it is somewhat more difficult to discern the types of quenching that occur, not only because of the competitive absorption, but also because of overlapping emission spectra from the two compounds. The results of experiments in which triphenylene was used in higher concentration and vice versa are reported in Table 14. In actual practice emission can occur from either species, and in fact, if quenching occurs it is more likely to appear from the quencher, or the substance in higher concentration. Absorption and emission spectra are presented for comparison in Figures 6, 7 and 8.

TABLE 14

Triphenylene and Stilbene Fluorescence Quenching Experiments

Stilbene conc. moles/ℓ.	Triphenylene conc. moles/ℓ.	λ Excit.	λ_{max} of Emitter	Intensity of Fluorescence at λ_{max}. Stilbene	Triphenylene
——	5×10^{-4}	3600	3575		18
		3420	(T.)		1360
		3100			456
0.25	——	3600	3650	210	
		3420	(S.)	5.6	
		3100		.6	
0.25	5×10^{-4}	3600	3650	248	
		3420	(S.)	8.6	
		3100		1.2	
		Samples with cis-stilbene were discarded because they contained a fluorescent impurity			
——	0.05	3600	3575		860
	——	3420	(T.)		23
10^{-3}	0.05	3600	3575		860
		3420	(T.)		17.4

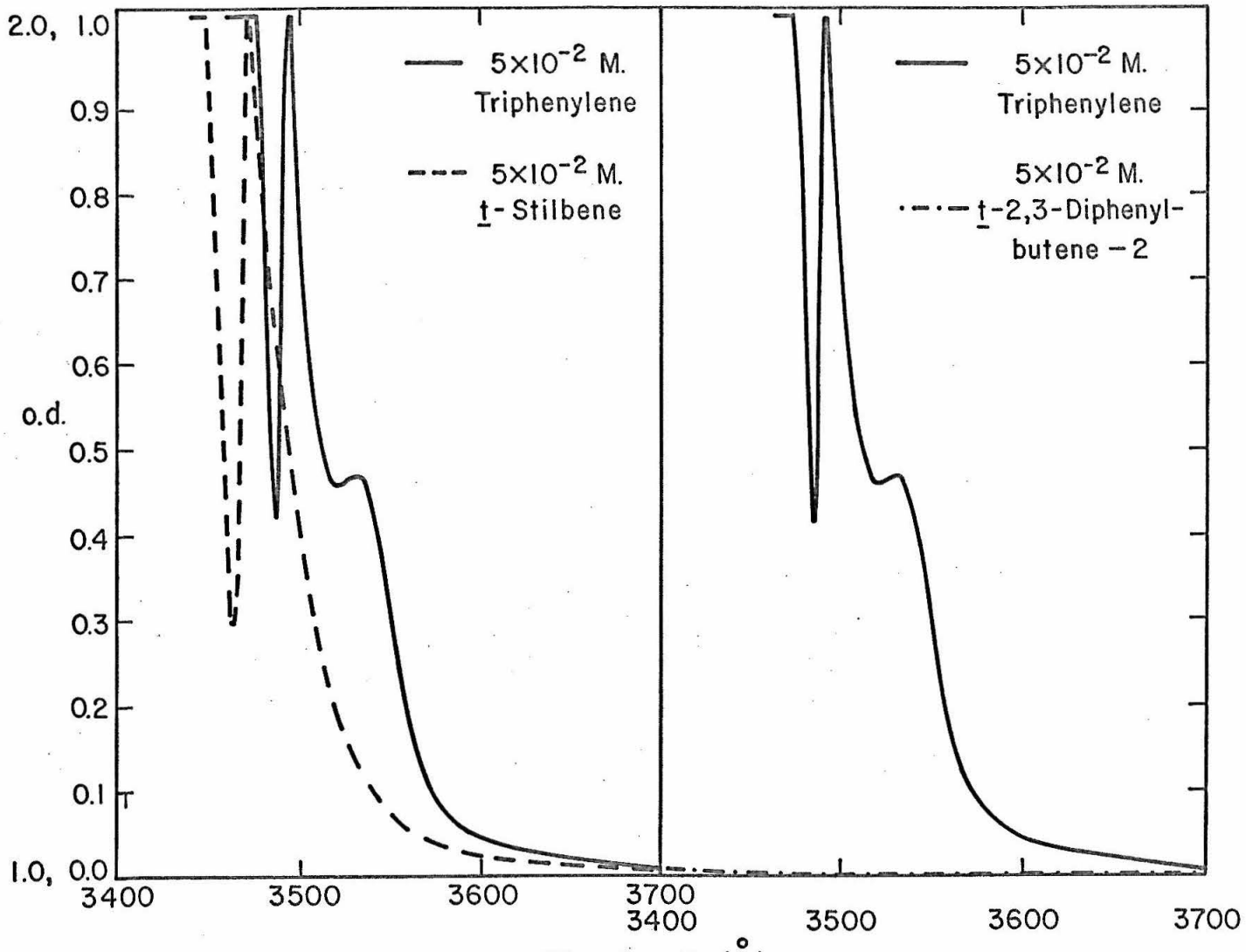

2.0, 1.0
0.9
0.8
0.7
0.6
o.d.
0.5
0.4
0.3
0.2
0.1
1.0, 0.0
3400
3500
3600
3700
5×10⁻² M. Triphenylene
5×10⁻² M. t-Stilbene
5×10⁻² M. Triphenylene
5×10⁻² M. t-2,3-Diphenyl-butene-2
3400
3500
3600
3700
Wavelength (Å)

Figure 6

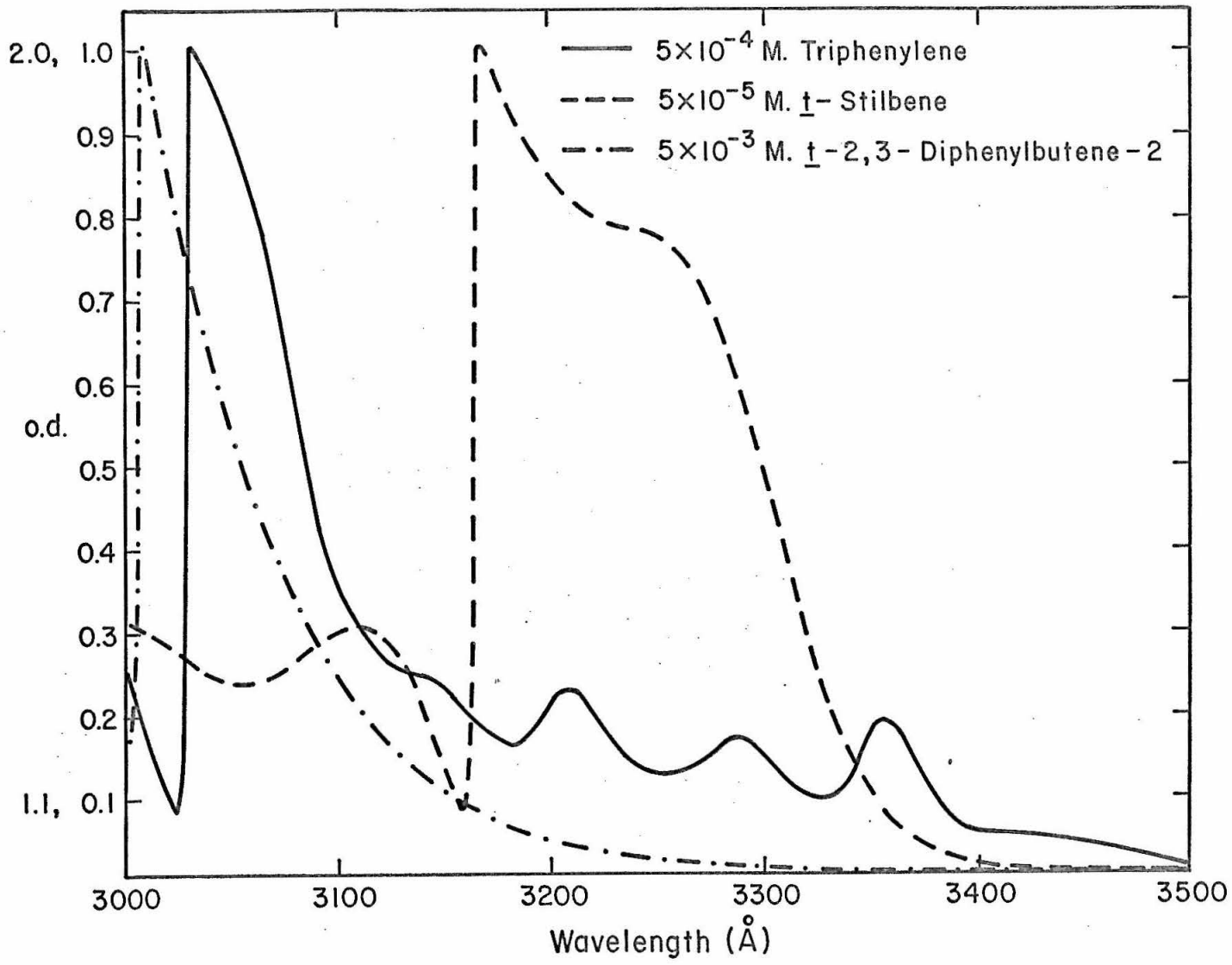

5×10^{-4} M. Triphenylene
5×10^{-5} M. t- Stilbene
5×10^{-3} M. t-2,3- Diphenylbutene-2
2.0, 1.0
0.9
0.8
0.7
0.6
o.d.
0.5
0.4
0.3
0.2
1.1, 0.1
3000
3100
3200
3300
3400
3500
Wavelength (Å)

Figure 7

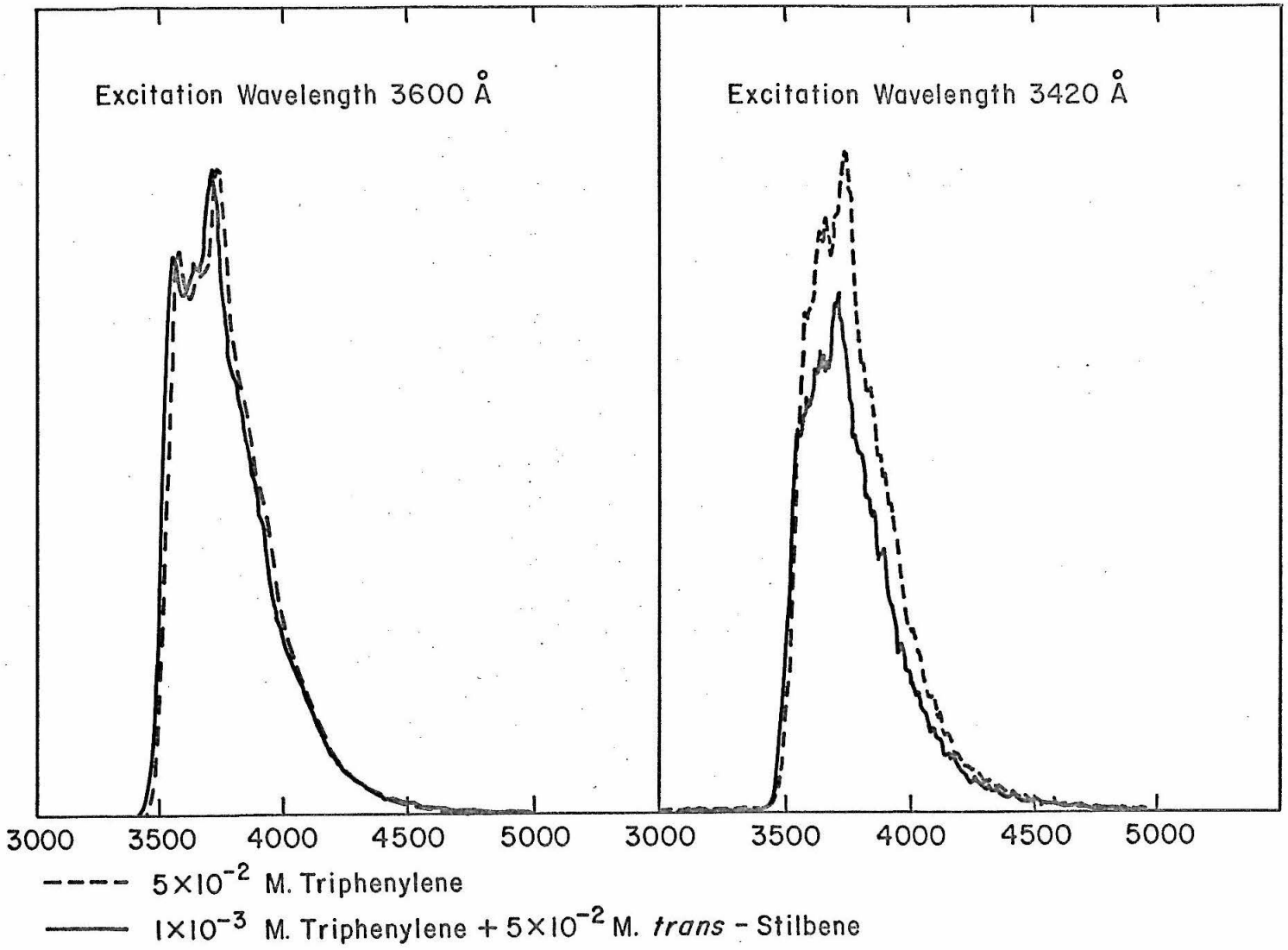

Excitation Wavelength 3600 Å
Excitation Wavelength 3420 Å
3000
3500
4000
4500
5000
3000
3500
4000
4500
5000
---- 5×10⁻² M. Triphenylene
—— 1×10⁻³ M. Triphenylene + 5×10⁻² M. trans - Stilbene

Figure 8

Several complicating features of the table should be pointed out. The letters in column four, which indicate the emitting species, are assigned to that substance whose emission dominates the spectrum. In practice the spectra were identically superimposable on one or the other of the substrates. The intensities obtained from triphenylene and trans-stilbene at the two concentrations can't be easily correlated, because at low concentrations absorption into the long wavelength tail will be negligible, but will become sizeable at higher concentrations. Also, the shape of the emission spectrum and thus the relative intensities at any given excitation wavelength, will depend strongly on the extent of reabsorption of the emission which is, of course, a function of the concentration. Furthermore, the excitation wavelength is not a highly reproducible value, and all solutions of group 1 were irradiated at the same time and group 2 at a different time.

At 3600 Å the triphenylene extinction coefficient is about twice that of trans-stilbene. At 3420 Å the extinction coefficients are equal. By 3100 Å in a solution of equal concentrations, stilbene gets 98.5% of the light. Therefore, in experiments with triphenylene in low concentrations and stilbene as quencher it is impossible to determine whether triphenylene is quenched or not since nearly all the light is absorbed by stilbene. It will therefore be assumed that the 2,3-diphenylbutene-2 experiment predicts the results for the stilbene system, i.e., no quenching of triphenylene by stilbene. However, in the case with stilbene in low concentration and triphenylene as quencher, 2% of the light is put directly into stilbene, which emits 4.5 times as efficiently under the experimental conditions. Therefore, some emission should be seen from

the stilbene. As it is, however, the triphenylene emission may be slightly decreased in intensity but shows none of the distortion which would be anticipated from a mixture of the two emissions. It would appear from these experiments that triphenylene quenches stilbene fluorescence but that this quenching does not lead to fluorescence in triphenylene. It is therefore concluded that if any quenching occurs in these systems that it occurs with triphenylene as a quencher but not with stilbene as quencher. This is consistent with the work being done by Stephenson which implies that triphenylene is not quenched as effectively as other aromatic hydrocarbons by conjugated dienes.

The work described above was done in undegassed solutions and therefore cannot be considered to be more than qualitatively indicative. The results obtained are consistent with the fact that the lowest singlet of triphenylene has a lower excitation energy than does the lowest excited singlet of stilbene. The first maximum of triphenylene is at ~ 3525 Å and that of stilbene is at ~ 3275 Å (46,47).

These results will be used to discard a singlet mechanism in which a complex is formed from excited state triphenylene and ground state stilbene, but cannot be used to exclude the reverse possibility.

The second set of experiments attempted to sensitize or quench the singlet or triplet processes preferentially. Benzophenone was used as the primary absorber of light, with concentrations being chosen so that the ketone would be expected to transfer triplet energy to the triphenylene, with the latter then finally transferring to stilbene. The concen-

trations were 0.05 M. benzophenone, 0.05 M. triphenylene and 0.005 M. stilbene. Transfer directly from benzophenone to stilbene should occur only 10% of the time. In other solutions piperylene was used in ~ 0.1 M. concentration as a triplet quencher. Greater concentrations might also result in singlet quenching. Even under these conditions more triplets were apprehended by piperylene than by stilbene so as to reduce the relative effectiveness of a triplet reaction as compared to a singlet reaction. The results, shown in Tables 15 and 16 are somewhat difficult, but not impossible, to interpret. Values for the photostationary states obtained in the presence of benzophenone and acetophenone alone (irradiated with 3660) are presented below for comparison.

TABLE 15

Selective Quenching Experiments with the Triphenylene-Stilbene System

	*0.05 M.T.†,‡	0.05 M.T., 0.05 M.B.†	*0.05 M.T., 0.05 M.P.‡	*0.05 M.T., 0.1 M.P., 0.05 M.B.†
0.005 M. *trans*-stilbene	67.4 (3130) 57.5 (3660)	57.8 ± 1.8	75.9 ± 2.4	60.7 ± 1.3 (% *cis*)
0.005 M. *cis*-1,2-diphenylpropene	57.9 ± 1.1	57.4 ± 1.6	58.8 ± 1.3	58.7 ± 1.5 (% *cis*)
0.005 M. *trans*-1,2-diphenylpropene	58.6 ± 1.2	58.2 ± 1.1	57.6 ± 1.4	58.9 ± 1.2 (% *cis*)
0.005 M. *trans*-2,3-diphenylbutene-2	79.8 ± .4	78.6 ± .9	85.3 ± .6	77.3 ± .8 (% *trans*)

†Irradiated with uranium glass filter (3660 Å).

‡Irradiated with pyrex filter (3130 Å).

*T = triphenylene, B = benzophenone, P = piperylene.

TABLE 16

Approximate Theoretical Values for Above Data

	~ p.s.s. Calculated for 0.05 M. sens., 0.005 M. substrate[a]	~ p.s.s. Calculated for 0.005 M. substrate and triplet quencher[b]	p.s.s. Observed for 0.005 M. substrate 0.05 M. sens.
Stilbene[d]	80.4% cis	90% cis	
1,2-Diphenylpropene[d]	58.0% cis	72% cis	58.3% cis
2,3-Diphenylbutene-2[d]	60.0% trans	70% trans	79.8% cis

	~ p.s.s. Calculated for sensitized process[c]
Stilbene[d]	61.6% cis
1,2-Diphenylpropene[d]	54.6% cis
2,3-Diphenylbutene-2[d]	60.2% trans

[a] Calculated using Equation 3.3.

[b] Calculated using Equation 3.3 with the assumption that a triplet quencher is equivalent to $\epsilon_{sens.} = 0$ (since stilbene triplets are not effectively quenched with the exception of the trans-stilbene triplet to a slight degree.

[c] Calculated from Equation 3.3 assuming $\epsilon_{stilbenes} = 0$.

[d] These calculations are effected in their accuracy by not only the computational approximations but also the fact that a narrow band pass filter was not used in the irradiations.

TABLE 17

Photostationary States Observed in the Presence of Acetophenone and Benzophenone (3660 Å)

	0.05 M. Acetophenone	0.05 M. Benzophenone
0.05 M. stilbene	59.2% cis	59.6% cis
0.05 M. 1,2-diphenylpropene	54.2% cis	55.9% cis†
0.05 M. 2,3-diphenylbutene-2	—	77.4% trans

†Later results by the author and Valentine indicate that 60% is a better value.

These values are in surprisingly good agreement with the values in Table 15, columns 2 and 4, considering the difference of a factor of ten in the stilbene concentrations. The photostationary states for the quenching experiments which contained piperylene are further complicated by the formation of numerous unidentified side-products.

Most of the ambiguities about the above data result from the fact that it was not possible to adjust the relative concentrations of stilbene, triphenylene and the various external sensitizers and quenchers in such a manner as to eliminate effectively all but one process at a time. It should also be noticed in this regard that there appears to be a degeneracy in all the results for 1,2-diphenylpropene. The photostationary state seems to be nearly equivalent to that shown in Figure 4 of 60.5 ± 1.1 for 0.005 M. % cis 1,2-diphenylpropene and 0.05 M. triphenylene, regardless of the presence or absence of added sensitizers or quenchers. It is not entirely clear at the present time whether this degeneracy indicates that the 1,2-diphenylpropene concentration is always the domin-

ant factor in the relative cis and trans isomerization rates, or whether there was merely an accidental crossing of all the various concentration dependence at this value.

In the case of stilbene there appears to be some difference in the % cis depending on whether the irradiation was conducted at 3130 Å or 3660 Å, as was shown in the first column, first row of Table 15. The 3130 Å value is more cis-rich than the 3660 Å value as would be expected from a normally increased proportion of direct stilbene isomerization at 3130 Å. Since the quenching experiments indicate that the triphenylene singlet is unquenched, any singlet mechanism can account for the anomalous behavior only as it originates from excited stilbene singlets. Therefore, a real wavelength dependence of this nature would lend weight to a triplet mechanism. However, these values were obtained from only one sample used as a check. Since triphenylene absorbs very weakly at 3660 Å, the 3660 Å tube may well not have reached the stationary state. Also this wavelength dependence is not appreciable for 1,2-diphenylpropene or 2,3-diphenylbutene-2 (the values in the first column of Table 15 were averaged since they were all within experimental error of each other), very little weight will be placed on the stilbene observation.

Possible Complicating Features

A disturbing alternative possibility for this system has been the conceivable presence of some impurity which reacts with stilbene, with itself, or with triphenylene in the presence of light to give a new sensitizer which takes over control of the reaction at some point after the beginning. The single bit of evidence in favor of this alternative is a slight reversal of the direction of the isomerization under somewhat pro-

longed irradiation of solutions containing 2,3-diphenylbutene-2. In solutions initially containing 100% trans; the concentration of cis builds up for a time, then slowly reverts partially to trans. Table 18 shows this phenomenon.

TABLE 18

Isomerization Reversal under Prolonged Irradiation

[Triphenylene]	[2,3-Diphenylbutene-2]	Time (days)	% trans	Total Change
0.05 M.	0.05 M.	2	87.1	1.4%
"		3	87.8	
"		4	88.5	
0.025 M.		4	88.1	1.7%
		7	88.0	
		10	89.8	
0.01 M.		4	89.9	1.8%
		7	91.3	
		10	91.7	
0.005 M.		4	89.9	0.9%
		7	89.8	
		10	90.8	

Similar reversals, although less precisely documented have also been observed with 1,2-diphenylpropene as substrate. In order to check the consistency of results as a function of sensitizer purity (it being assumed that an impurity in any one of the stilbenes would not give uniform discrepancies in all, or would produce anomalies with other sensitizers), several samples of triphenylene were used to sensitize the reaction. The results of the check are reported in Table 19.

Another feature associated with the reversal in 1,2-diphenylpropene only is the very occasional appearance of a very small amount of

new product appearing shortly after cis on the v.p.c. trace. Presence of this extraneous peak does not seem to effect the quantitative average of isomer ratios from various tubes but is invariably accompanied by a much higher degree of scatter between otherwise identical tubes.

TABLE 19

Effect of Triphenylene Purification on Photostationary States

Substrate	Method of Triphenylene Purification	Photostationary State
c-1,2-Diphenylpropene	Hinton zone-refined	38.1 ± 2.2% cis
	Treated with norite, recrystallized twice from EtOH	40.1 ± .3% cis 39.9 ± .5% cis
t-1,2-Diphenylpropene	Treated with norite, recrystallized twice from EtOH	42.6 ± .6% cis
t-2,3-Diphenylbutene-2	Hinton zone-refined	88.0 ± 2.2% trans
	Recrystallized by Fox from EtOH	87.5 ± .8% trans
	DeBoer zone-refined	87.8 ± .4% trans

It is evident from these figures that triphenylene purity is not the dominant factor in the nature of the results which have been discussed.

Discussion

At the present time it would seem unprofitable to try to distinguish between the alternatives of modifying the classical (i.e., determined by energy differences between donor and acceptor only) energy transfer rates by means of an actual excited state complex, or by imposing relative orientation requirements on the interacting molecules

which effect the relative probabilities of various modes of simple energy transfer. Each model possesses certain advantages both of a practical and an aesthetic nature.

Excited State Complexes

There are several possible kinetic schemes which can incorporate most of the data, starting either from a triplet state or a singlet state complex. A few representative schemes will be discussed for which detailed algebraic solutions are presented in Appendix I. No mixtures of singlet or triplet processes were included in the study, not because they are not most likely to represent the real situation, but because they give rise to unwieldy solutions.

SCHEME I

Singlet Complex

$$S + h\nu \xrightarrow{k_1} {}^1S \qquad (3.4.1)$$

$$t + h\nu \xrightarrow{k_2} {}^1t \qquad (3.4.2)$$

$$c + h\nu \xrightarrow{k_3} {}^1c \qquad (3.4.3)$$

$$S + {}^1t \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} {}^1S + t \qquad (3.4.4)$$

$$S + {}^1c \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} {}^1S + c \qquad (3.4.5)$$

$${}^1S + t \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} {}^1St \qquad (3.4.6)$$

$${}^1S + c \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} {}^1Sc \qquad (3.4.7)$$

$$S + {}^1t \underset{k_{-8}}{\overset{k_8}{\rightleftarrows}} {}^1St \qquad (3.4.8)$$

$$^1St \xrightarrow{k_9} S + t \qquad (3.4.9)$$

$$^1St \xrightarrow{k_{10}} S + c \qquad (3.4.10)$$

$$^1c + S \underset{k_{-11}}{\overset{k_{11}}{\rightleftarrows}} {}^1Sc \qquad (3.4.11)$$

$$^1Sc \xrightarrow{k_{12}} S + c \qquad (3.4.12)$$

$$^1Sc \xrightarrow{k_{13}} S + t \qquad (3.4.13)$$

$$^1t \xrightarrow{k_{14}} t \qquad (3.4.14)$$

$$^1c \xrightarrow{k_{15}} c \qquad (3.4.15)$$

$$^1S \xrightarrow{k_{16}} S \qquad (3.4.16)$$

$$^1S \xrightarrow{k_{17}} {}^3S \qquad (3.4.17)$$

Of these steps k_{-4}, k_{-5}, k_{-6}, k_{-7} can all be discarded on the basis of the quenching experiment in which 2,3-diphenylbutene-2 was shown to have no effect on the triphenylene fluorescence efficiency. Steps involving k_{-6}, k_{-7}, k_{-8} and k_{-11} can be discarded on the basis that there was no temperature dependence of the photostationary state. Step 16 can be ignored since for triphenylene $\varphi_f + \varphi_{ic} = 1$. The simplified mechanism can then be written:

SCHEME II

$$S + h\nu \xrightarrow{k_1} {}^1S \qquad (3.5.1)$$

$$t + h\nu \xrightarrow{k_2} {}^1t \qquad (3.5.2)$$

$$c + h\nu \xrightarrow{k_3} {}^1c \qquad (3.5.3)$$

$$^1t + s \xrightarrow{k_4} {}^1S + t \qquad (3.5.4)$$

$$^1c + S \xrightarrow{k_5} {}^1S + c \qquad (3.5.5)$$

$$S + {}^1t \xrightarrow{k_6} {}^1St \qquad (3.5.6)$$

$$S + {}^1c \xrightarrow{k_7} {}^1Sc \qquad (3.5.7)$$

$$^1St \xrightarrow{k_8} S + t \qquad (3.5.8)$$

$$^1St \xrightarrow{k_9} S + c \qquad (3.5.9)$$

$$^1Sc \xrightarrow{k_{10}} S + c \qquad (3.5.10)$$

$$^1Sc \xrightarrow{k_{11}} S + t \qquad (3.5.11)$$

$$^1t \xrightarrow{k_{12}} t \qquad (3.5.12)$$

$$^1c \xrightarrow{k_{13}} c \qquad (3.5.13)$$

$$^1S \xrightarrow{k_{14}} {}^3S \qquad (3.5.14)$$

The solution to the simplified mechanism presented in Scheme II is the following:

$$\frac{[t]}{[c]} = \frac{k_3k_7k_{11}}{k_2k_6k_9} \frac{[k_8 + k_9]}{[k_{10} + k_{11}]} \frac{[(k_4 + k_6)[S] + k_{12}]}{[(k_5 + k_7)[S] + k_{13}]} \qquad (3.5.15)$$

Although this solution predicts a mild sensitizer concentration dependence, which is observed, it does not predict any stilbene concentration dependence. It therefore must be concluded to be inadequate, however, a minor modification in the given scheme may be added which does introduce the desired dependence:

SCHEME III

$$^1St + c \xrightarrow{k_{15}} {}^1Sc + t + \text{Scheme II} \qquad (3.5.16)$$

The reverse reaction was excluded on the basis that the photostationary state is trans rich at high stilbene concentrations. The solution to Scheme III is

$$[c] = \frac{-\left[\frac{BT + A}{a(S)} + \frac{D}{b(S)}\right] + \sqrt{\left(\frac{BT + A}{a(S)} + \frac{D}{b(S)}\right)^2 + \frac{4AT}{a(S)}\left(\frac{E}{b(S)} - \frac{B}{a(S)}\right)}}{2\left(\frac{E}{b(S)} - \frac{B}{a(S)}\right)} \qquad (3.6)$$

where T = total stilbene concentration

a(S) and b(S) = linear functions of sensitizer concentration

The simplest triplet scheme which would appear to be consistent with the data is the following:

SCHEME IV

$$S + h\nu \xrightarrow{k_1} {}^1S \qquad (3.7.1)$$

$${}^1S \xrightarrow{k_2} {}^3S \qquad (3.7.2)$$

$$t + h\nu \xrightarrow{k_3} {}^1t \qquad (3.7.3)$$

$${}^1t \xrightarrow{k_4} {}^3t \qquad (3.7.4)$$

$$c + h\nu \xrightarrow{k_5} {}^1c \qquad (3.7.5)$$

$${}^1c \xrightarrow{k_6} {}^3c \qquad (3.7.6)$$

$${}^3S + t \xrightarrow{k_7} {}^3St \qquad (3.7.7)$$

$${}^3S + c \xrightarrow{k_8} {}^3Sc \qquad (3.7.8)$$

$${}^3t \xrightarrow{k_9} p \qquad (3.7.9)$$

$${}^3c \xrightarrow{k_{10}} p \qquad (3.7.10)$$

$$p \xrightarrow{k_{11}} t \qquad (3.7.11)$$

$$p \xrightarrow{k_{12}} c \qquad (3.7.12)$$

$$^3St \xrightarrow{k_{13}} S + t \qquad (3.7.13)$$

$$^3St \xrightarrow{k_{14}} S + p \qquad (3.7.14)$$

$$^3Sc \xrightarrow{k_{15}} S + c \qquad (3.7.15)$$

$$^3Sc \xrightarrow{k_{16}} S + p \qquad (3.7.16)$$

$$^3St + c \xrightarrow{k_{17}} {}^3Sc + t \qquad (3.7.17)$$

$$^1t \xrightarrow{k_{18}} t \qquad (3.7.18)$$

$$^1c \xrightarrow{k_{19}} c \qquad (3.7.19)$$

Here again dissociation of the complex was excluded on the basis of the null temperature effect. Such steps as,

$$^3St \longrightarrow S + {}^3t \qquad (3.7.20)$$

$$^3S + t \longrightarrow S + p \qquad (3.7.21)$$

$$^3S + c \longrightarrow S + {}^3c \qquad (3.7.22)$$

$$^3S + c \longrightarrow S + p \qquad (3.7.23)$$

i.e., the normal sensitization process were left out in order to ease the calculation. Solution of the equation even so is quartic in [c] in terms of various powers of the total stilbene concentration. Although this is not inconsistent with the data, its analytic form is difficult to visualize. Setting k_{17} equal to zero simplifies it to a quadratic, i.e., similar to the equivalent singlet mechanism. Another means of simplification to a quadratic is merely to replace steps 9 and 10 by:

SCHEME V

$$^3t + S \xrightarrow{k_9} {}^3St \qquad (3.7.9)$$

$$^3c + S \xrightarrow{k_{15}} {}^3Sc \qquad (3.7.10)$$

However, this seems to be in poor judgement on an energetic basis. The complex formed will of necessity have energy equal to or less than the constituents. In the "equal to" case the intermediates would not be likely to be considerably different from the triplet process, and dissociation of the complex could occur. In the less than case, not enough energy would be left to form the phantom triplet, at least in the interaction with cis, which is equivalent to interaction with the phantom. The calculation was included only to see from which steps the high-order concentration dependence resulted.

Kinetically, it is clear that one cannot distinguish between a singlet and a triplet mechanism for this system. Therefore, in actuality, a mixture of two types of complexes would probably give rise to a solution of similar form to those presented above. It is not completely clear whether this extension would hold for a mixture of complex formation and normal sensitization, however, although it is possible.

However, one may incorporate the data gleaned from the quenching experiments (Tables 15, 16, and 17) with the observations of Fox on the direct and sensitized photodecomposition of azo-1-cyanocyclohexane to form the prejudical conclusion that the singlet complex is more consistent with the data. Comparing columns two and four of Table 15 with the acetophenone and benzophenone sensitization data given in Table 17 one finds that these results are very similar, implying that in the absence

of direct excitation of either stilbene or triphenylene, triphenylene is a normal high energy sensitizer. The worst deviations from normality are those obtained from the experiments in which a triplet quencher was added (column 3). The point with 2,3-diphenylbutene-2 is trans rich compared to the value which would have been predicted from the concentration variation in Figure 5. The stilbene point is more cis rich than the 0.05 M. value but this would be according to expectation from a concentration variation resembling that for 2,3-diphenylpropene. The extent to which the mixture is more cis rich in the presence of piperylene than it is in its absence, at the same stilbene concentration, could reflect either the extent to which the anomaly is accentuated by removing the compensating "normal" triplet process, or could reflect the importance of the "normal" direct absorption into stilbene at a concentration where the unknown anomalous reaction which produces trans is beginning to be less important. In the decomposition of azo-1-cyclohexane, the quantum yield of decomposition in the presence of triphenylene is inappreciably changed from that of the direct process, i.e., the singlet initiated decomposition. Furthermore, coronene, the analogous sensitizer to triphenylene with non-analogous behavior, can be (and was) irradiated at 3660 Å, where the stilbenes do not absorb, unlike triphenylene. The fluorescence quenching experiments have minimized the possibility of unexplained reaction from singlet sensitizer; it might be enlightening to see whether irradiating coronene solutions at 3130 Å would induce the triphenylene-like results. On the other side, there appears to be no particular point which favors the formation of a triplet complex.

Reduced Probability Factors for Energy Transfer

As was previously mentioned, triphenylene has an emission intensity distribution which is significantly different from that of most aromatic hydrocarbon sensitizers. Lamola (48) suggested that the abnormally long radiationless lifetime and the small effect of deuterium substitution on the observed phosphorescence lifetime could be attributed to localization of the electronic energy in the interior of the molecule. Such centralization of the excitation could reduce the relative importance of C–H vibrations with respect to C–C modes.

In the present study the internalization of energy could effect the isomerization product ratios by causing different amounts of energy to be transferred depending on the various relative orientations of stilbene and triphenylene. For instance, variations on the following mechanism could be envisaged.

$$^3T + S \longrightarrow T + {}^3S \qquad \text{(S is stilbene, T is triphenylene)} \qquad (3.8.1)$$

$$^3T + S \longrightarrow T^* + p^* \qquad (3.8.2)$$

$$^3T + S \longrightarrow T^{**} + p \qquad (3.8.3)$$

Unfortunately, however, the only simple way to introduce a concentration effect into such a scheme would be by inclusion of such terms as these in the above mechanism, requiring the interaction of several

$$^3T + c + t \longrightarrow p^* + p + T \qquad (3.8.4)$$

$$^3T + 2t \longrightarrow 2p + T \qquad (3.8.5)$$

$$^3T + 2c \longrightarrow 2p^* + T \qquad (3.8.6)$$

nearest neighbors. Again relative rate differences would depend not only on the energy requirements for non-vertical excitation but also on the mutual orientations of the reactants. Although this explanation has considerably greater aesthetic appeal than the complex formation alternative, it is in practicality somewhat considerably less palatable. Perhaps the real solution incorporates features of both.

PART 4

FREE RADICAL INDUCED PHOTOISOMERIZATION IN THE STILBENE SYSTEMS

Introduction

Referring to Figure 3 it is readily apparent that a considerable number of points cannot be fitted onto a plot with one maximum, the basis for the original structured Saltiel plot. Although there is no obvious immediate explanation for some of the discrepancies, careful examination shows that the vast majority of these points fall into the three previously mentioned classes of sensitizers, the 1,2 diketones, quinones and halogen containing aromatics with low triplet energies. Two of these classes, the 1,2 diketones and the quinones, are well known to form adducts with olefins, which will be discussed and referenced and all three are known to photodissociate or to undergo photoreduction to give various types of free radicals. Discussions of a few of these reactions relevant to this work would seem to be in order.

The photochemistry of duroquinone has been studied extensively by Bridge and Porter (49) using flash photolytic techniques. They concluded that the following kinetic scheme adequately describes the system in a variety of solvents.

$$Q + h\nu \xrightarrow{k_1} {}^1Q \qquad (4.1.1)$$

$${}^1Q \xrightarrow{k_2} {}^3Q \qquad (4.1.2)$$

$${}^3Q \xrightarrow{k_3} Q \qquad (4.1.3)$$

$${}^1Q + RH \xrightarrow{k_4} QH\cdot + R\cdot \qquad (4.1.4)$$

$${}^3Q + RH \xrightarrow{k_5} QH\cdot + R\cdot \qquad (4.1.5)$$

$$2QH\cdot \xrightarrow{k_6} Q + QH_2 \qquad (4.1.6)$$

$$QH\cdot \xrightarrow{k_7} Q\cdot^- + H^+ \qquad (4.1.7)$$

$$2Q\cdot^- \xrightarrow{k_8} Q + Q^{2-} \qquad (4.1.8)$$

$$Q\cdot^- + H^+ \xrightarrow{k_9} QH\cdot \qquad (4.1.9)$$

$$K = \frac{[Q\cdot^-][H^+]}{[QH\cdot]} \qquad (4.1.10)$$

In the neutral and/or hydrogen-donating environments involved in the work to be discussed, only the first six equations need be considered, since K was determined to be 1.2×10^{-6} moles/ℓ. Surprisingly, 80% of the semiquinone formation occurred through reaction 4.1.4 or by means of the singlet state. By direct observation of step 4.1.7 in ethanol it was concluded that the primary photochemical process is indeed hydrogen abstraction and not an electron transfer process. Similar studies with anthraquinone and 1,4-napthoquinone showed that these compounds behaved similarly to duroquinone.

Koizumi has shown (51) that several common dyes can hydrogen-abstract in a similar manner to produce photo-reduced radical transients. These include eosin and acridine, both of which produce fairly trans rich photostationary states when used as sensitizers in all the stilbene systems.

The scheme for acridine reduction in degassed solutions is as follows:

$$A + h\nu \xrightarrow{k_1} {}^*A$$

$${}^*A + RH_2 \xrightarrow{k_2} AH\cdot + RH\cdot$$

$$AH\cdot + RH\cdot \xrightarrow{k_3} A + RH_2$$

$$AH\cdot + RH\cdot \xrightarrow{k_4} AH_2 + R$$

$$AH\cdot + AH\cdot \xrightarrow{k_5} AH_2 + A$$

$$RH\cdot + RH\cdot \xrightarrow{k_6} HRRH \text{ or } R + RH_2$$

Dimerization was not an important side reaction under the conditions of their study. The quantum yield of the overall reaction is temperature independent favoring neglect of k_3 and a choice between $k_4 + k_5$. Since no dimerization occurs k_4 is favored over k_5. Aerated solutions give a more complex scheme.

Eosin apparently is simply photoreduced to the semiquinone radical. The reaction is nearly totally quenched in aerated solutions. In both cases the intermediate was determined to be a semiquinone rather than a triplet on the basis of long-lived color changes in the solution in the absence of oxygen and by consideration of the measured or estimated lifetimes of the transients.

Further work done by Moore and Waters (50) on the photochemical reactions of various quinones in cumene would appear to substantiate the generality of these types of reactions. Extended irradiation of phenanthraquinone, chloranil and 1,4-napthoquinone in cumene produced the following products:

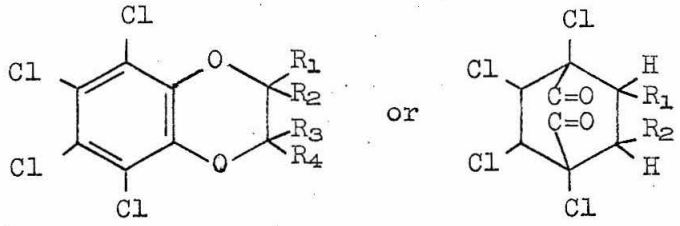
TABLE 20

Photochemistry of Some Quinones in Cumene

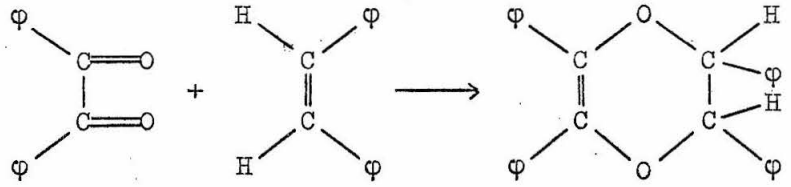
phenanthraquinone	chloranil	1,4-napthoquinone
phenanthraquin-hydrone 85%	tetrachloro-quinol 63%	1,4-dihydroxy-naphthalene 40%
α-methylstyrene	α-methylstyrene	α-methylstyrene
2,3-dimethyl- 2,3-diphenyl-butene 3%	hydrogen chloride	

Quinol ethers were not obtained in any case, a point which was verified for chloranil in the present study.

Substituted ortho-quinones, such as 2,3,4,5-tetrachloro-ortho-benzoquinone, react with olefins to give addition compounds of two types (52):

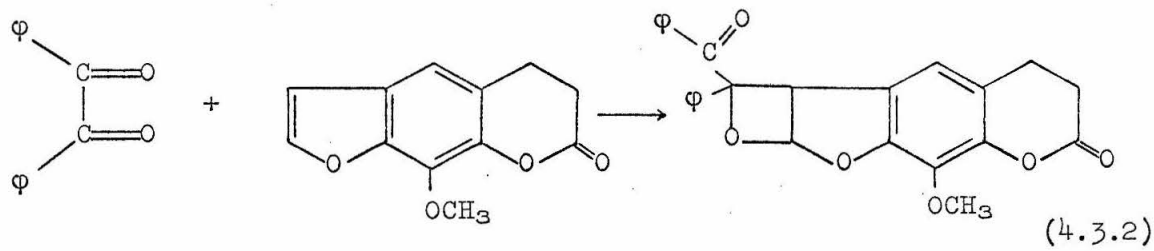


Schönberg and Mustafa (53) were the first to report reactions between 1,2-diketones, e.g., benzil, and olefins, among them stilbene, to give dioxenes:



(4.3.1)

In some special cases it has been shown (54) that benzil also will produce oxetanes, e.g.

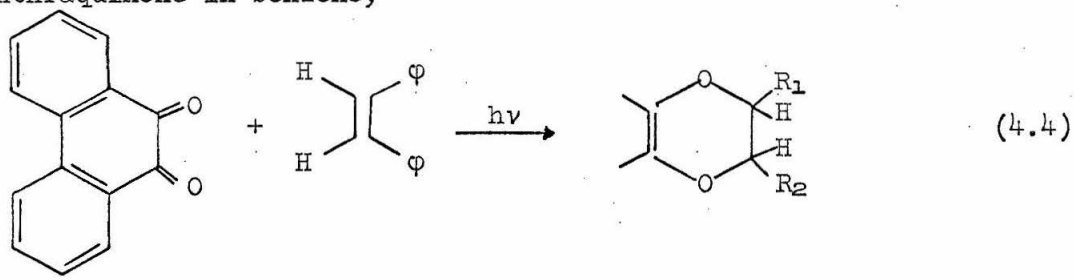


(4.3.2)

The former reaction is successful enough with a wide variety of compounds to have preparative value. A completely analogous set of reactions has been studied for orthoquinones such as 9,10-phenanthraquinone.

Clearly there is a vast array of possible reactions among the sensitizers of interest with the various stilbenes and the solvents. In spite of these multitudinous complications it was hoped in the early studies that under the reaction conditions of the experiments, these side reactions would proceed in low enough yield to compete only ineffectually with cis-trans isomerization, or by different enough and slow enough mechanisms to be unrelated to it.

Bohning and Weiss (55) have been the first to attempt formulation of a mechanism which describes the extent of direct implication of the sensitizer in the establishment of low energy equilibration of cis-trans isomers as modified by side reactions. Their system is stilbene-phenanthraquinone in benzene,



(4.4)

for which the quantum yields, Φ_A, of adduct formation under ideal conditions were reasonably low (Φ_A(cis) = .14, Φ_A (trans) = .066). It was determined that with an excess of stilbene the disappearance of quinone followed the rate law,

$$-\frac{d[Q]}{dt} = \Phi_A I_{abs.} \tag{4.5}$$

over most of the course of the reaction. The quantum yields were discussed in terms of two possible mechanisms, the Pfundt-Schenck mechanism and one modeled after the Hammond-Saltiel mechanism. The Schenck mechanism is presented below.

$$Q \overset{h\nu}{\rightleftharpoons} {}^1Q \tag{4.6.1}$$

$${}^1Q + C{=}C \longrightarrow X \tag{4.6.2}$$

$$X + Q \longrightarrow A + Q \tag{4.6.3}$$

$$X \longrightarrow C{=}C + Q \tag{4.6.4}$$

The authors expanded steps two and four into separate steps for the cis and trans isomers which gives

$$\Phi_A = \frac{a[Q]}{b+[Q]} \tag{4.7}$$

where a and b are the proper constants in the presence of a large excess of olefin.

The Schenck mechanism was discarded on the basis of several important points. First of all, the above mechanism predicts a sensitizer concentration dependence, which is not experimentally observed. Objection was made to the necessity of assigning a specific quenching role to the ground state sensitizer (a common objection to Schenck-type

mechanisms which can be easily eliminated) on the grounds that any other type of molecule, such as solvent, olefin, or adduct should also be able to perform this function. Reversibility of step one was discarded as a result of the invariance of Φ_A with olefin concentration. However, the prime objection to the Schenck mechanism was that even, with modification to include the isomerization, it still leads to equality of Φ_A from the cis- and trans-isomers.

The Hammond type mechanism was vastly more successful in correlating their results.

$$Q + h\nu \xrightarrow{k_1} {}^1Q \qquad (4.8.1)$$

$${}^1Q \xrightarrow{k_2} Q \qquad (4.8.2)$$

$${}^1Q \xrightarrow{k_3} {}^3Q \qquad (4.8.3)$$

$${}^3Q + t \xrightarrow{k_4} X \qquad (4.8.4)$$

$${}^3Q + c \xrightarrow{k_5} X \qquad (4.8.5)$$

$${}^3Q + t \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} {}^3t + Q \qquad (4.8.6)$$

$$X \xrightarrow{k_7} A \qquad (4.8.7)$$

$$X \xrightarrow{k_8} p + Q \qquad (4.8.8)$$

$$t \xrightarrow{k_9} p \qquad (4.8.9)$$

$$p \xrightarrow{k_{10}} t \qquad (4.8.10)$$

$$p \xrightarrow{k_{11}} c \qquad (4.8.11)$$

(Refer to Equation 4.4 for the structure of A.)

They did not include,

$$^3Q + c \xrightarrow{k_{12}} Q + {}^3c \qquad (4.8.12)$$

$$^3c \xrightarrow{k_{13}} p \qquad (4.8.13)$$

on the basis of energy requirements, but gave no reason for ignoring

$$^3t \xrightarrow{k_{14}} t \quad \text{or} \qquad (4.8.14)$$

$$^3Q + c \xrightarrow{k_{15}} Q + p\ , \qquad (4.8.15)$$

the unimolecular quenching of cis or the non-vertical process. It was suggested, justifiably, that the above mechanism represents a fair compromise between simple energy transfer and a biradical intermediate. For stable sensitizers the collision complex merely breaks up to isomerized olefin and sensitizer. Classical energy transfer to trans-stilbene gives the needed difference between the cis and trans yields for adduct formation. A single intermediate, X, is predicated on the identity of final products starting from either isomer.

Application of the steady state hypothesis for excited states gives,

$$-\frac{d[Q]}{dt} = \frac{I_{abs.}\ K_3\ K_7\ (k_4\ R + k_5)}{(k_4 + ak_6)\ R + k_5} \qquad (4.9)$$

where

$$K_3 = \frac{k_3}{k_2 + k_3}$$

$$K_7 = \frac{k_7}{k_7 + k_8}$$

$$a = \frac{k_9}{k_9 + k_{-6}[Q]} \simeq 1$$

$$R = \text{initial isomer ratio } \left(\frac{[t]}{[c]}\right)$$

A temperature dependence of K_7 was observed, which indicates that the decay of X to p and Q is an activated process. The above experiments indicated a "photostationary" [trans][cis] ratio of 0.7 which supposedly represents a balance between adduct formation and isomerization. The isomer ratio would be expected to be much richer in cis, solely on the basis of energy considerations. However, since adduct formation occurs more rapidly from cis than trans, the amount of trans is higher than could be predicted from a pure energy transfer mechanism. However the photostationary balance is only a pseudo stationary state since the material balance between stilbene and adduct is not conserved.

Bohning and Weiss do not consider the formation of semiquinone radicals which, by adding to and eliminating from stilbene, compete with photochemical isomerization to decrease the [cis]/[trans] ratio. They did, however, report a build up of unidentified side products which absorb in the 400 mμ region. The present work indicates that this mode of isomerization is an important one.

Results

Quinones and Halogen Containing Compounds

Electron paramagnetic resonance studies were made on a few selected systems by Wood and Coyne in order to establish the presence and determine the structure of any free radicals in the stilbene-sensitizer-benzene systems under conditions used for the isomerization studies. In the case of the quinones which were investigated, good experimental evidence was obtained for the presence of neutral semiquinone type radicals in sizeable concentrations. Figures 9, 10, and 11 show comparisons between the experimental spectra and the theoretical reconstruction of the spectra for the p-benzoquinone, methyl-p-benzoquinone and duroquinone neutral radicals. Table 21 shows the measured proton hyperfine splitting constants for these spectra. Of the two nonequivalent forms of the methyl-p-benzoquinone semiquinone radical only one appeared to exist in measurable concentrations under the conditions of study.

The structure of radicals obtained from the halogen compounds are less conclusive. Eosin might be expected to give free radicals from hydrogen abstraction as a result of its quinoid type structure, or to behave like 9,10-dibromoanthracene to give bromine atoms and some aromatic radical structure of unknown composition. The halogen radicals would be expected to be too short-lived to be able to be seen directly, so probably the observed spectra represent a composite of products from a variety of primary and secondary photochemical steps.

The effects of added stilbene or 2,3-diphenylbutene-2 to the quinone spectra are quite interesting. Changes are induced in the

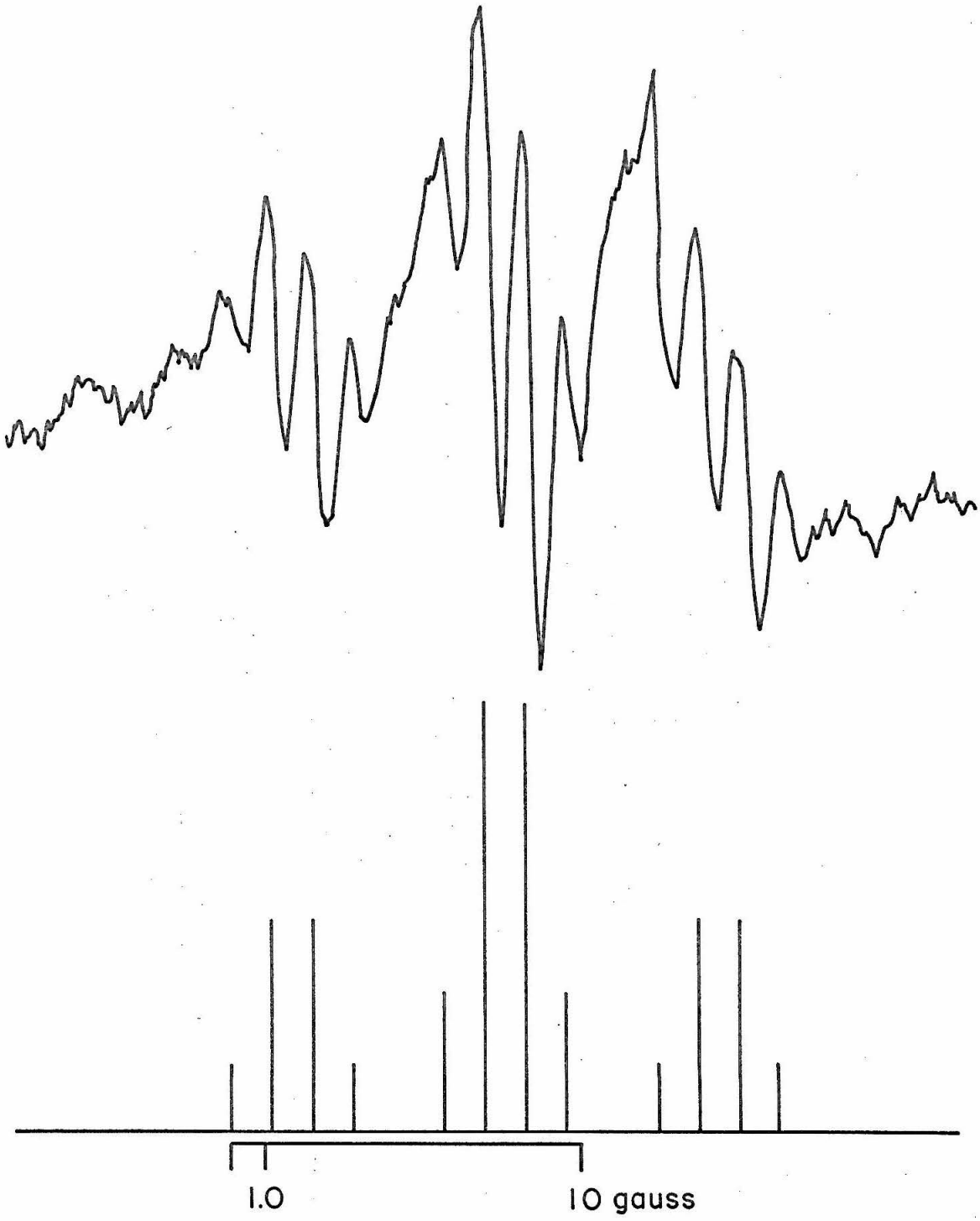


Figure 9 Neutral p – Benzosemiquinone Radical

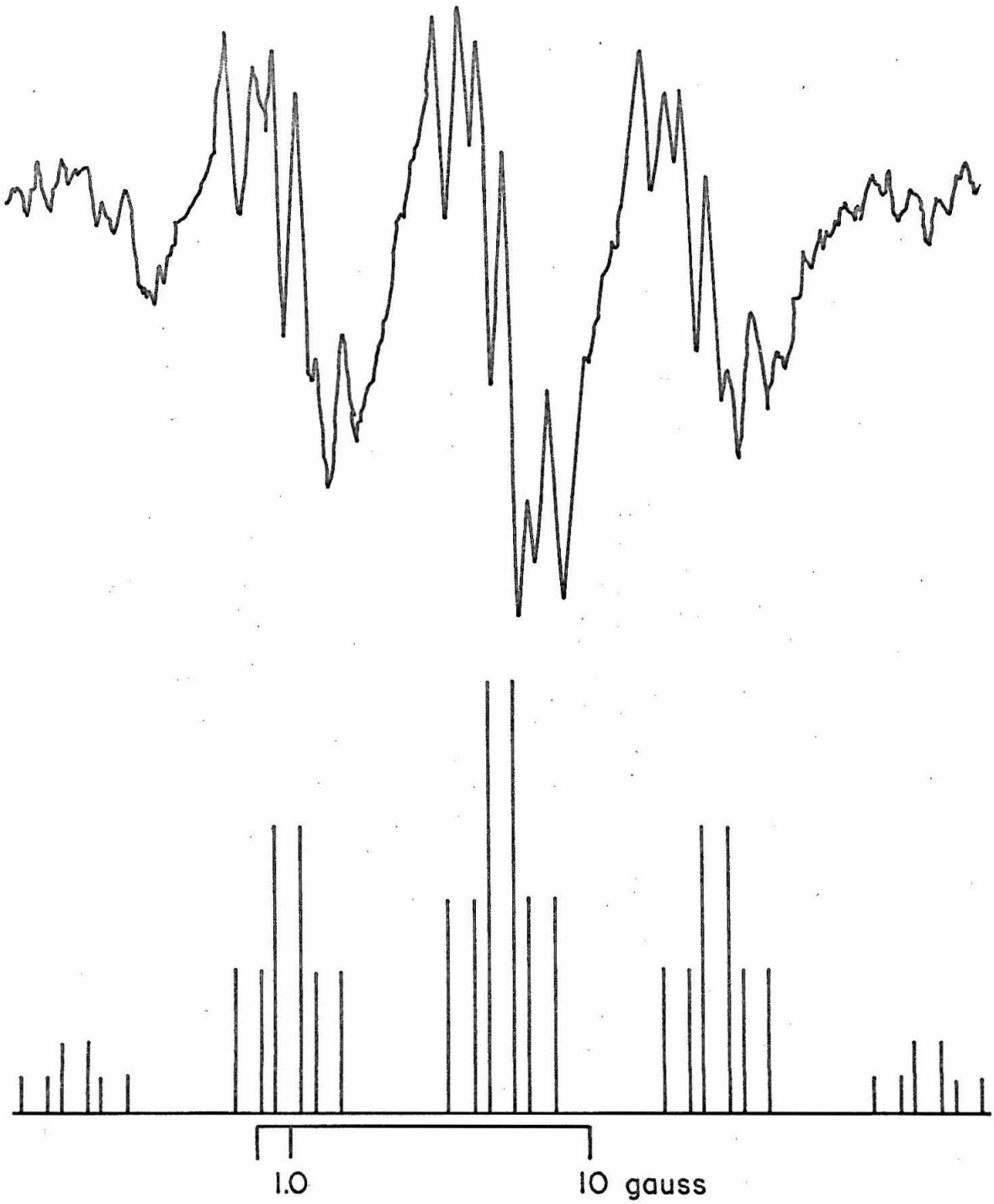


Figure 10 Neutral Methyl-p-Benzosemiquinone Radical Species I

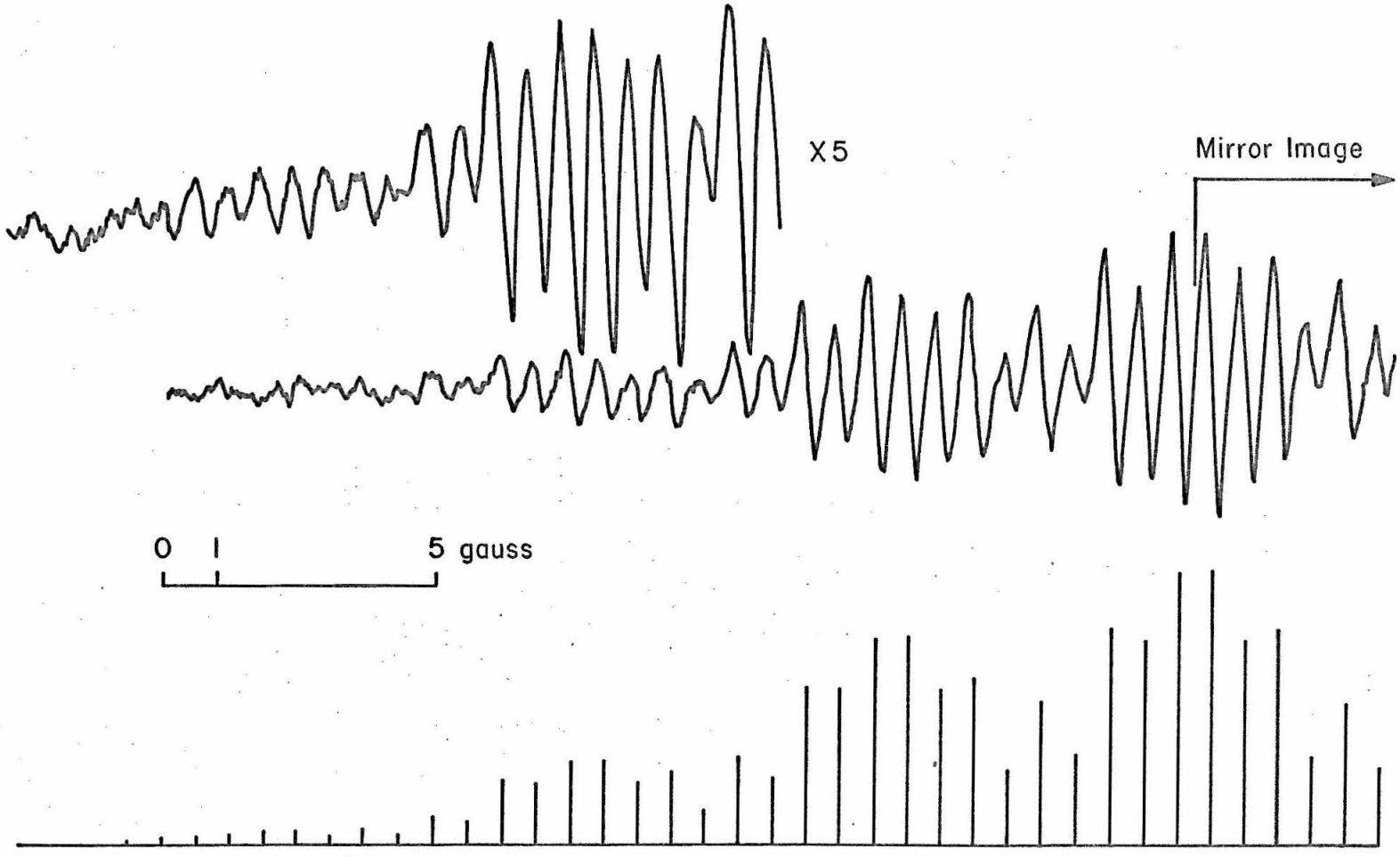
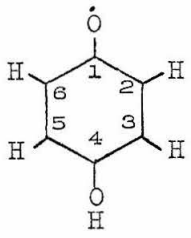


Figure 11 Neutral 2,3,5,6-Tetramethyl-p-Benzosemiquinone Radical

TABLE 21

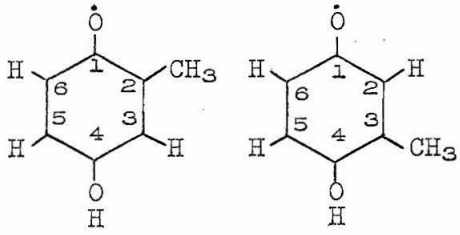
Observed Proton Splitting Constants



$a_2^{\dagger} = a_6 = 6.15 \pm .1$ gauss

$a_3 = a_5 = 1.15 \pm .05$ gauss

$a_4 = 1.15 \pm .05$ gauss



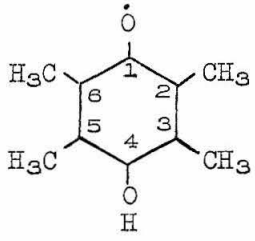
Species II was not observed

Species I

$a_2 = a_6^{\ddagger} = 6.08 \pm .1$ gauss

$a_3 = a_5 = 1.15 \pm .05$ gauss

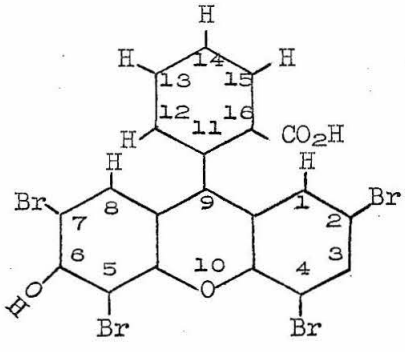
$a_4 = .75 \pm .05$ gauss



$a_2 = a_6 = 5.55 \pm .10$ gauss

$a_3 = a_5 = 1.227 \pm .020$ gauss

$a_4 = 0.604 \pm .010$ gauss



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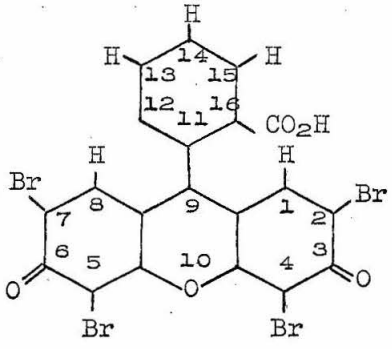


II

TABLE 21--continued

† The a's represent the splitting that occurs as a result of coupling between the unpaired electron on the numbered carbon atom and the nuclear spins of the protons joined to that carbon atom, according to McConnell's rule $a = Qp$

where Q is characteristic of the nature of the group joined to the carbon atom of interest and p is the probability of finding the unpaired electron on that carbon atom.

‡ $a_2 = a_6$ because the second order effect of the adjacent methyl group on Q can be considered to be small.

steady state concentrations of the free radicals, which, of course, would have to be the case if the radicals are entering directly into the isomerization process. A further effect is inhibition of the polymerization or other forms of degradation of the sensitizer solutions, indicating that the radicals are stabilized by stilbene. However, addition of the stilbenes has no effect on the nature of the free-radical species produced, with the one exception of stilbene and chloranil. Here a permanent free radical with a one line signal is formed on irradiation. This may be in some manner correlated with the fact that stilbene and chloranil form a highly colored, strong, charge transfer complex in their ground states.

Table 22 shows some semiquantitative effects of added stilbene or 2,3-diphenylbutene-2 concentration on the durosemiquinone spectrum. Table 23, also taken from the research report of Wood, gives some further results of the effect of added stilbenes on the nature of the e.p.r. signals obtained.

TABLE 22

Effect of Added Stilbene on Durosemiquinone Signal Intensities

Duroquinone conc. moles/ℓ.	Substrate conc. moles/ℓ.	Relative Steady State Radical Concentration
0.05	———	100
0.05	0.05 2,3-diphenyl-butene-2	406
0.05	0.05 stilbene	110
0.05	0.005 stilbene	320
0.005	0.05 stilbene	37

TABLE 23

Effects of Added Stilbenes on E.P.R. Spectra in Benzene

Solute 0.05M No.1	Solute 0.05M No.2	Solute 0.05M No.3	Light Dependence	Stability† under Irradiation	Relative Signal Strength	Hyperfine Splittings‡
p-Benzoquinone			Partly	Poor	Weak	A 3 line pattern was light dependent but was obscured by a permanent broad signal which built up with irradiation.
p-Benzoquinone	p-Benzohydroquinone		Yes	Fair	Fair	A 3 line pattern was seen with each line consisting of 4 components. The broad underlying signal builds up more slowly than in the sample without HQ.
p-Benzoquinone	p-Benzohydroquinone	Stilbene	Yes	Good	Fair	Fair resolution allows assignment. There are 3 groups with intensity 1:2:1. Each is split into 4 lines of intensity distribution 1:3:3:1. All large splittings = 6.15 gauss, all small splittings = 1.15 gauss, all line widths are 0.5 gauss (max. homogeneity of 6" magnet)
p-Benzoquinone	0-0-Dideutero-p-Benzohydroquinone	Stilbene	Yes	Good	Fair	It looks as if deuterated semiquinone constitute one-half of the total semiquinone present compared to the above sample which contains no deuterium.
p-Benzoquinone*				Poor	Very weak	Too weak to resolve
p-Benzoquinone*	2,3-Diphenylbutene-2		No	Poor	Very weak	Small permanent signal
Methyl-p-benzoquinone	Stilbene				Very weak	
Methyl-p-benzoquinone	2,3-Diphenylbutene-2		Yes	Fair	Fair	There are 3 or 5 groups with 6.08 gauss splitting, each group split unequally into 6 lines. The center pair = 0.68 gauss; the splitting from outer to nearest one of center pair = 1.15 gauss; the splitting from one of center pair to nearest line is less than 0.40 gauss. g = 2.0046
Methyl-p-benzoquinone	Methyl-p-hydroquinone	Stilbene	Yes	Fair	Fair	Same as above
Methyl-p-benzoquinone	Methyl-p-hydroquinone	DBP**	Yes	Fair	Fair	Same as above
Phenyl-p-benzoquinone	Stilbene		Yes	Fair	Weak	There are 2 lines, unsymmetrical, with about 16 gauss overall and about 4 gauss between components. It is not clear if there are two radicals or just one. g = 2.0036 for high field component
Phenyl-p-benzoquinone	2,3-Diphenylbutene-2		Yes	Fair	Weak	Similar to above but now some hyperfine structure is visible on each component
Phenyl-p-benzoquinone	Phenyl-p-hydroquinone	Stilbene	Yes	Poor	Fair	After long irradiation only one broad line is left
Phenyl-p-benzoquinone	Phenyl-p-hydroquinone	DBP	Yes	Fair	Fair	Each of the lines appears now to be composed of 10 smaller lines with splittings 0.43 gauss
Chloranil			Yes	Fair	Good	No hyperfine structure was resolved
Chloranil	Stilbene		No	Fair	Good	Permanent radicals are formed but no hyperfine structure could be resolved
Chloranil	2,3-Diphenylbutene-2		Yes	Fair	Good	No hyperfine structure was resolved
Duroquinone			Yes	Excellent	Excellent	There are 7 groups of lines with intensities 1:6:15:20:15:6:1, a = 5.5 gauss. Each group consists of at least ten lines which overlap with neighboring groups, a = 0.6 gauss
Duroquinone	2,3-Diphenylbutene-2		Yes	Excellent	Excellent	Identical with above
Duroquinone	Stilbene		Yes	Excellent	Excellent	Identical with above
Duroquinone	Stilbene 0.005M		Yes	Excellent	Excellent	Identical with above
Duroquinone 0.005M	Stilbene		Yes	Excellent	Excellent	Identical with above
9,10-Dibromoanthracene			Yes	Good	Very weak	None resolved
9,10-Dibromoanthracene	Stilbene		Yes	Good	Very weak	None resolved
9,10-Dibromoanthracene	2,3-Diphenylbutene-2		Yes	Good	Very weak	None resolved
Eosin			Yes	Fair	Fair	Three lines, splitting 3.3 gauss, central line width 1.7 gauss
Eosin	Stilbene		Yes	Fair	Fair	Three lines, splitting 3.0 gauss, central line width 1.7 gauss
Eosin	2,3-Diphenylbutene-2		Yes	Fair	Fair	Three or five lines, splitting 3.46 gauss, intensity distribution 1:6:14:6:1, the resolution is better than in the above spectrum
Naphthoquinone	Stilbene		Yes	Poor	Weak	Three lines with about 4 gauss splitting, 35 gauss overall width
Fluorenone	2,3-Diphenylbutene-2		Yes	Fair	Weak	25 gauss overall spectrum width. No hyperfine structure was resolved
Stilbene			No	Fair	Very weak	Very weak permanent signal
2,3-Diphenylbutene-2			No	Fair	Very weak	Very weak permanent signal
Anthracene			Yes	Good	Weak	25 gauss overall, unresolvable

†Determined primarily by visual inspection and secondarily by change in E.P.R. Signal with continued irradiation.

‡For original spectrum numbers refer to David E. Wood, Research Report.

*Solvent was p-xylene.

**2,3-Diphenylbutene-2.

Since it was clearly established that for the quinones the semiquinone neutral radicals are the prime paramagnetic species in solution--the triplet states being either in too low a concentration or too short-lived to be observed, it was attempted to establish their relationship to the isomerization process by photochemical means. It would be expected from equations 1.7 and 1.8 that the relative accessibility of hydrogen atoms would affect the balance between the two mechanisms in the case of 2,3-diphenylbutene-2 and the rate of isomerization in the case of stilbene. Therefore, studies were initiated to measure the "photostationary" states and relative rates of isomerization in a solvent containing no easily abstractable hydrogen atoms (benzene) and one containing a source of readily available hydrogen atoms (cumene).

The results of the "photostationary" state measurements are shown in Table 24.

Considering cumene, 2,3-diphenylbutene-2, or duroquinone to be sources of hydrogen atoms, it is apparent that the ultimate "steady states" obtained are affected by the availability of abstractable hydrogen atoms.

It is important to note that these pseudo steady state ratios are by no means photostationary in the true sense of the word. In nearly all cases (particularly with the quinones) the initial tendency is to produce a fairly high concentration of cis isomer, then after prolonged irradiation to revert to a long-term photostationary state very rich in the trans isomer. Such results strongly imply that a new substance builds up in concentration over a period of time and ultimately controls either, or both, chemical and photochemical equilibria.

TABLE 24

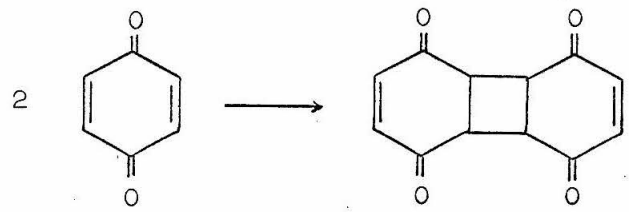
"Photostationary" States of Stilbene Systems in the Presence of Quinone and Halogen Containing Sensitizers

Substrate 0.05 moles/ℓ.	Sensitizer 0.05 moles/ℓ.	Solvent	p.s.s. (% cis) 3660†	4045†	4358†
Stilbene	Benzoquinone	Benzene	63.3 ± 1.8		20.5
		Cumene	53.2 ± .8		
	Duroquinone	Benzene	73.6 ± .9		71.4
		Cumene	73.1 ± 1.1		
	Chloranil	Benzene	2.2 (2 days)‡ 2.8 (3 days) 9.0 (4 days)		
		Cumene	82.1 ± .6		
			p.s.s. (% trans)		
	9,10-Dibromoanthracene	Benzene	0		
		Cumene	18.1 (2 days)‡ 21.3 (3 days) 41.4 (4 days)		
2,3-Diphenylbutene-2	Benzoquinone	Benzene	90.8 ± .6		
		Cumene	92.3 ± .8		
	Duroquinone	Benzene	95.9 ± .5		
		Cumene	95.0 ± .5		
	Chloranil	Benzene	93.3 ± .7		
		Cumene	94.3 ± .2		
	9,10-Dibromoanthracene	Benzene	69.4 ± .4		
		Cumene	73.0 ± .6		

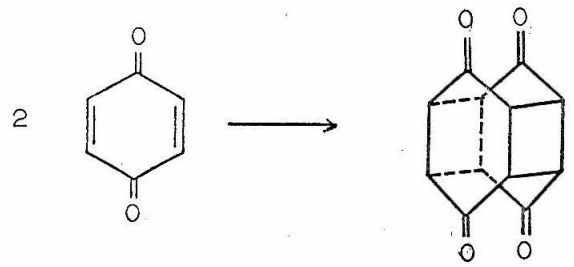
†Wavelength of irradiation.

‡When the isomer ratios change markedly over the period of irradiation the successive values are reported.

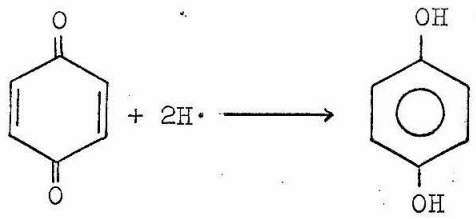
From the quinones several candidates are available.



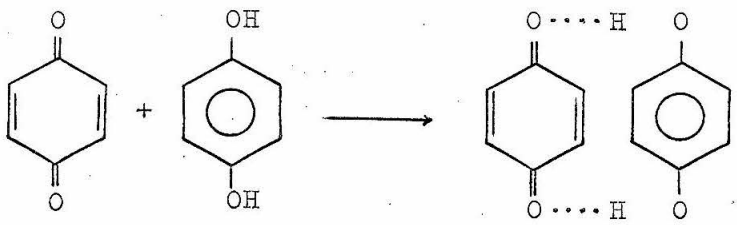
(4.10.1)



(4.10.2)



(4.10.3)



(4.10.4)

The latter two compounds are only very slightly soluble, but are the most likely to be formed in the reaction. The triplet energy of hydroquinone would be expected to be higher than that of benzoquinone, as a consequence of loss of the $n \rightarrow \pi$ triplet states. Assuming the effect is purely photochemical in origin, the result of a new compound of higher triplet energy would produce an increasingly <u>cis</u> rich state in stilbene and an increasingly <u>trans</u> rich state in 2,3-diphenylbutene-2. The re-

sults of irradiation of solutions of stilbenes in the presence of hydroquinone are shown in Table 25.

TABLE 25

Hydroquinone Sensitized Isomerization of the Stilbenes, [HQ] = Saturated

Substrate 0.05 M.	Filter System	Solvent	p.s.s. % trans)
Stilbene	U	Benzene	92.1 ± .7
	U	Cumene	92.0 ± .7
2,3-Diphenyl-butene-2	U	Benzene	99.3 ± .2
	U	Cumene	98.8 ± .1

If the above numbers truly represent a photostationary state of the stilbene systems with hydroquinone, it is highly probable that the trans rich state represents the result of some sort of sensitization by either hydroquinone or quinhydrone. However, for hydroquinone the extinction coefficient at 3660 Å is very low ($\epsilon \simeq 0.1$), and although quinhydrone absorbs strongly far into the visible, it is exceedingly insoluble in benzene.

The most interesting aspect of the photostationary measurements is the formation of a product in the 2,3-diphenylbutene-2 system which has a v.p.c. retention time only slightly greater than that of the trans isomer. This product could easily be 2,3-diphenylbutene-1 which would result from rearrangement of the 2,3-diphenylbutenyl radical.

TABLE 26

Product Formation from 2,3-Diphenylbutene-2 in the Presence of Some Radical Sensitizers

Sensitizer	Solvent	$\frac{p}{p + c + t} \times 100$
Chloranil	Benzene	53.2 ± 1.1
	Cumene	8.9 ± .7
9,10-Dibromoanthracene	Benzene	1.6 ± .5
	Cumene	0

Since 2,3-diphenylbutene-1 was not commercially available, or easily prepared from commercially available starting materials, studies were made on the 1,2-diphenylpropene--2,3-diphenylpropene system in order to establish that this type of rearrangement can occur under the experimental conditions. The mixtures of products obtained from long term irradiation of 1,2-diphenylpropene, and 2,3-diphenylpropene in the presence of a few of these sensitizers are found in Table 27.

The results are not possible to interpret in more than a semi-quantitative manner, as side reactions destroy the substrates during the course of the reaction. The degree of destruction is a function of solvent and starting material as well as of irradiation time. Clearly a sizeable proportion of the 2,3-diphenylpropene gets converted to the 1,2-isomers regardless of the solvent. Apparently the equilibrium lies far toward the stilbene rather than toward the benzylstyrene side. It is not clear whether this represents a chemical or a photochemical equilibrium. The cis isomer appears to be formed only slowly by the reaction,

TABLE 27

Product Equilibration in Diphenylpropene System

Substrate	Sensitizer	Solvent	Irradiation Time (days)	$\frac{c}{c+t} \times 100$	$\frac{p}{c+t+p} \times 100$
2,3-Diphenyl-propene	Chloranil	Benzene	2	30.7 ± .7	85.4 ± 2.0
			3	28.3 ± 4.5	81.1 ± 1.0
			3.5	30.0 ± 2.9	71.6 ± 4.1
		Cumene	3	indeter.	97.2 ± .3
			4	44.2	93.1 ± .5
			4.5	50.6 ± 2.1	91.3 ± .3
t-1,2-Diphenyl-propene	"	Benzene	2	88.1 ± 3.3	0
			3	89.4 ± 2.9	0
			3.5	89.1 ± .9	0
		Cumene	3	91.2 ± .4	0
			4	90.6 ± .3	0
			4.5	89.9 ± .9	0
c-1,2-Diphenyl-propene	"	Benzene	2	—	—
			3	—	—
			3.5	—	—
		Cumene	3	87.3	trace
			4	87.4 ± .1	"
			4.5	87.6 ± .8	"
2,3-Diphenyl-propene	9,10-Di-bromoan-thracene	Benzene	2	27.2 ± .9	75.8 ± 2.9
			3	22.9 ± .8	63.1 ± 2.0
			3.5	28.3 ± 2.0	70.8 ± 2.9
		Cumene	3	40.3 ± .3	83.2 ± .2
			4	68.8 ± 1.6	64.3 ± .7
			4.5	70.1 ± .8	53.2 ± .3
t-1,2-Diphenyl-propene	"	Benzene	2	18.9 ± .9	2.6 ± .8
			3	19.1 ± .4	3.9 ± .9
			3.5	18.4 ± .8	2.8 ± .6
		Cumene	3	32.1 ± 1.1	0
			4	37.8 ± 1.8	0
			4.5	42.2 ± .1	0
c-1,2-Diphenyl-propene	"	Benzene	2	—	—
			3	—	—
			3.5	—	—
		Cumene	3	27.1 ± .6	~1%
			4	31.7 ± .2	~1%
			4.5	38.6 ± 1.0	~1%

implying that interconversion of trans-1,2-diphenylbutene and 2,3-diphenylbutene is more rapid than production of cis- 1,2-diphenylbutene. Bradshaw (56) reports 26.5% cis with 9,10-dibromoanthracene as sensitizer. He too noted the formation of small amounts of 2,3-diphenylpropene. The fact that this equilibrium is approached with the three isomers in the diphenylpropene system strongly implies that the process observed in the diphenylbutene system is the same.

Relative rates of isomerization and product formation in the stilbene and 2,3-diphenylbutene-2 systems indicate that the hydrogen abstraction capabilities of the solvent strongly effect the equilibration process. Photochemical differences between benzene and cumene irradiated at 3600 Å could not possibly have any major effect. The relative isomerization rates for quinoid and halogen-containing sensitizers are given in Table 28.

Several points should be noted about the data given to this point. First of all the steady state mixtures being approached are not generally related in any way to equilibration mixtures. Secondly, the formation of rearranged products appears to be quenched by cumene. This is consistent with the hydrogen abstraction mechanism, since in cumene more hydrogen atoms will be abstracted from the solvent, thus decreasing the efficiency of abstraction from a substituted stilbene. The lack of thermal equilibration mixtures, taken with the possible wavelength dependence of certain of the photostationary states alluded to in Table 24 indicate the possibility of a two quantum process being needed to complete isomerization by the addition-elimination mechanism. This possibility will be discussed in greater detail later.

TABLE 28

Relative Rates of Isomerization as a Function of Solvent

Substrate	Sensitizer	Solvent	Irradiation Time (hrs.)	$\frac{c}{c+t} \times 100$	$\frac{p}{c+t+p} \times 100$
2,3-Diphenyl-	Benzoquinone	Benzene	2	27.6 ± .5	—
			4.5	30.6 ± .0	—
			9.5	29.4 ± .3	—
		Cumene	2	12.8 ± .4	—
			4.5	14.3 ± .3	—
			9.5	14.2 ± .4	—
	Duroquinone	Benzene	2	——	—
			4.5	4.8 ± .4	—
			9.5	4.6 ± .4	—
		Cumene	2	4.4 ± .2	—
			4.5	4.7 ± .4	—
			9.5	5.1 ± .4	—
	Chloranil	Benzene	2	22.3 ± .2	38.3
			4.5	19.9 ± .5	33.4
			9.5	16.3 ± .5	29.4
		Cumene	2	8.5 ± .1	9.4
			4.5	8.4 ± .3	10.2
			9.5	7.3 ± .2	8.8
	9,10-Dibromo-anthracene	Benzene	2	5.5 ± .1	—
			4.5	11.6 ± .4	—
			9.5	31.0 ± .5	—
		Cumene	2	3.4 ± .1	—
			4.5	7.8 ± .1	—
			9.5	12.1 ± .7	—
	Eosin†	Benzene	3	——	—
			.5	99.9 ± .0	—
			1.75	99.9 ± .0	—
		Cumene	3	99.9 ± .0	—
			.5	99.95± .0	—
			1.75	99.0 ± .0	—

†Not enough time was allowed to obtain any substantial quantity of isomerization.

TABLE 28--continued

Substrate	Sensitizer	Solvent	Irradiation Time (hrs.)	$\frac{c}{c+t} \times 100$	$\frac{p}{c+t+p} \times 100$
Stilbene	Benzoquinone	Benzene	7	15.2 ± .1	
			9	16.4 ± .2	
			25	21.1 ± .3	
		Cumene	7	17.3 ± .4	
			9	36.6 ± .1	
			25	49.5 ± .2	
	Duroquinone‡	Benzene	7	70.1 ± .1	
			9	68.6 ± .9	
			25	69.6 ± 1.4	
		Cumene	7	———	
			9	67.0 ± 1.4	
			25	67.9 ± .3	
	Chloranil	Benzene	7	3.1 ± .0	
			9	4.0 ± .1	
			25	4.9 ± .8	
		Cumene	7	3.0 ± .1	
			9	4.6 ± .2	
			25	7.9 ± .5	
	9,10-Dibromo-anthracene	Benzene	7	1.0 ± .2	
			9	.9 ± .4	
			25	———	
		Cumene	7	6.9 ± .2	
			9	———	
			25	16.7 ± .3	
	Eosin†	Benzene	3	99.2 ± .1	
			.5	99.6 ± .0	
			1.75	99.5 ± .0	
		Cumene	3	99.3 ± .0	
			.5	99.7 ± .0	
			1.75	99.6 ± .0	

†Not enough time was allowed to obtain any substantial quantity of isomerization.

‡These samples were stored in the dark for some weeks after irradiation but before analysis, therefore the results may not really indicate the photochemical rates.

An interesting feature of the relative rates in Table 28 deserves comment. At first glance, photostationary states appear to have been established in some of the cases. However, it seems imminently more reasonable to assume that these values are really the turn-around point between the short-term cis-rich and the long term trans-rich pseudo photostationary states. Although with stilbene the rate is slower in benzene than in cumene, the opposite is true with 2,3-diphenylbutene-2. The addition-elimination (Eq. 1.7) mechanism will be enhanced in cumene as a result of more efficient production of cumyl radicals. However, the hydrogen-abstraction mechanism (Eq. 1.8) should be weakened by the more rapid destruction of excited state quinones in cumene. Thus the hydrogen abstraction mechanism must be favored for the 2,3-diphenylbutene-2 system, as might be expected from steric hindrance to addition of a bulky radical.

1,2-Diketones

The experimental work done with these compounds has been similar to but more tentative than that done with the quinones and halogen containing compounds. Both relative rate measurements and a search for the rearrangement of the diphenylpropenes were made, the latter by Stephen P. Elliot. The effects with these sensitizers with a few exceptions are considerably smaller, if not insignificant compared to the previously studied compounds, as would be predicted from the smaller variance in the photostationary states from those which were expected. However, the rearrangement does occur. Differences in the relative rates were observed by approaching too close to the photostationary state of stilbene, despite the short irradiation periods. With 2,3-di-

phenylbutene-2 the necessity of starting from all trans had the same effect, since the ultimate equilibrium is so close to 100% trans that no appreciable spreading of the rates of isomerization could be anticipated. With the exception of one biacetyl sample which was irradiated 24 hrs., product formation was not measured since it constituted less than 1% of the reaction mixture.

The relative rate data are shown in Table 29 and the product formation data are presented in Table 30.

TABLE 29

Relative Rates of Isomerization as a Function of Solvent with 1,2-Diketone Sensitizers

Substrate	Sensitizer	Solvent	Irradiation Time (hrs.)	$\frac{c}{c+t} \times 100$	$\frac{p}{c+t+p} \times 100$
Stilbene	Benzil	Benzene	.5	87.8 ± .2	
			1.75	94.3 ± .2	
			3	94.0 ± .2	
		Cumene	.5	88.4 ± .4	
			1.75	94.0 ± .2	
			3	94.7 ± .1	
	β-Naphthil	Benzene	.5	68.6 ± .9	
			1.75	84.4 ± .1	
			3	83.9 ± .1	
		Cumene	.5	65.8 ± .2	
			1.75	84.5 ± .1	
			3	83.6 ± .2	
	Biacetyl	Benzene	.5	81.1 ± .1	
			1.75	89.3 ± .6	
			3	88.3 ± .1	
		Cumene	.5	80.2 ± .4	
			1.75	———	
			3	87.7 ± .3	
2,3-Diphenyl-butene-2	Benzil	Benzene	.5	93.8 ± .3	
			1.75	———	
			3	88.3 ± .1	
		Cumene	.5	94.5 ± .3	
			3	94.4 ± .2	
			24	93.5 ± .1	
	β-Naphthil	Benzene	.5	99.4 ± .0	
			1.75	98.8 ± .0	
			3	97.6 ± .1	
		Cumene	.5	99.1 ± .1	
			1.75	98.2 ± .1	
			3	96.6 ± .4	
	Biacetyl	Benzene	.5	91.5 ± .3	
			3	90.9 ± .3	
			24	91.3 ± .1	1.7
		Cumene	.5	91.5 ± .1	
			1.75	91.6 ± .4	

TABLE 30

Rearrangement of Diphenylpropenes under Irradiation of 1,2-Diketone Sensitizers

Substrate	Sensitizer	Solvent	Irradiation Time (days)	$\frac{c}{c+t} \times 100$	$\frac{p}{c+t+p} \times 100$
2,3-Diphenyl-propene	Benzil	Benzene	3	100	83
			4	100	77
			5	95	69
		Cumene	3	93	44
			4	83	51
			5	94	49
c-1,2-Diphenyl-propene	Benzil	Benzene	3	81	.4
			4	79	1.1
			5	82	.8
		Cumene	3	71	.7
			4	75	.4
			5	77	.4
2,3-Diphenyl-propene	Biacetyl	Benzene	3	9	97.8
			4	23	99.6
			5	9	97.8
		Cumene	3	5	99.7
			4	0	99.7
			5	0	99.1
c-1,2-Diphenyl-propene	Biacetyl	Benzene	3	90	.1
			4	78	.1
			5		
		Cumene	3	83	.1
			4	82	.1
			5	81	.2

Discussion

Attack by free radicals, either on the stilbene double bond, or on the methyl group hydrogen atoms of the substituted stilbenes, is sufficient to explain nearly all of the results presented in the previous section. A simple kinetic description for attack on the double bond and its desired quenching by cumene can be written as follows. The scheme can also be easily adapted to describe attack by a halogen atom.

$$Q + h\nu \xrightarrow{E} {}^1Q \qquad (4.11.0)$$

$${}^1Q + IH \xrightarrow{k_1} QH\cdot + I\cdot \qquad (4.11.1)$$

$${}^1Q + CH \xrightarrow{k_2} QH\cdot + C\cdot \qquad (4.11.2)$$

$${}^1Q \xrightarrow{k_3} {}^3Q \qquad (4.11.3)$$

$$QH\cdot + t\text{-}S \xrightarrow{k_4} QHS\cdot \qquad (4.11.4)$$

$$QH\cdot + c\text{-}S \xrightarrow{k_5} QHS\cdot \qquad (4.11.5)$$

$$QHS\cdot \xrightarrow{k_6} QH\cdot + t\text{-}S \qquad (4.11.6)$$

$$QHS\cdot \xrightarrow{k_7} QH\cdot + c\text{-}S \qquad (4.11.7)$$

$$QH\cdot + CH \xrightarrow{k_8} QH_2 + C \qquad (4.11.8)$$

$$2QH\cdot \xrightarrow{k_9} D \qquad (4.11.9)$$

$$2C\cdot \xrightarrow{k_{10}} C_2 \qquad (4.11.10)$$

$$2C\cdot \xrightarrow{k_{11}} M + C \qquad (4.11.11)$$

In the above, Q is a quinone, D is the quinone-hydroquinone complex, quinhydrone, I is some hydrogen-containing impurity and C is cumene.

It is possible to separate the above process from the sensitized process because, as was shown by Bridge and Porter's work, radical formation occurs through the singlet state. The quantum yield for formation of trans can be expressed by:

$$\Phi_t = \frac{k_6}{k_6 + k_7} \frac{(k_4[t\text{-}S] + k_5[c\text{-}S])[QH\cdot]}{(k_1[IH] + k_2[CH] + k_3)[^1Q]} \tag{4.12}$$

$$[QH\cdot] = \sqrt{\frac{k_1}{k_9}[^1Q][IH]} \quad \text{in benzene} \tag{4.13}$$

$$[QH\cdot] = \frac{k_2}{k_8}[^1Q] \quad \text{in cumene} \tag{4.14}$$

Therefore the ratio of the rates of production of the two isomers is:

$$\frac{\Phi_t \text{ (benzene)}}{\Phi_t \text{ (cumene)}} = \frac{k_8}{k_2} \frac{(k_2[CH] + k_3)}{(k_1[IH] + k_3} \sqrt{\frac{k_1}{k_9} \frac{[IH]}{[^1Q_B]}} \tag{4.15}$$

$$[^1Q] \text{ (in benzene)} = \frac{E}{k_1[IH] + k_3} \simeq 2 \times 10^{-15} \text{ moles}/\ell$$

One can substitute in the rate constants for production of the various radical and excited species, as determined by Bridge and Porter (57) for duroquinone, to get an estimate of the relative amounts of isomerization induced by addition-elimination in the two solvents. The level of aliphatic impurity in benzene was estimated to be 0.001%, or $\sim 10^{-4}$ M. The rate constants are:

$$k_1 = k_2 \simeq 5 \times 10^4$$

$$k_3 = 5 \times 10^5$$

$$k_8 \simeq 10^9$$

$$k_9 = 5 \times 10^8$$

The steps,

$$C\cdot + t\text{-}S \longrightarrow CS\cdot \qquad (4.16.1)$$

$$C\cdot + c\text{-}S \longrightarrow CS\cdot \qquad (4.16.2)$$

$$CS\cdot \longrightarrow t\text{-}S + C\cdot \qquad (4.16.3)$$

$$CS\cdot \longrightarrow c\text{-}S + C\cdot \qquad (4.16.4)$$

$$QH\cdot + IH \longrightarrow QH_2 + I\cdot \qquad (4.16.5)$$

were disregarded for ease of calculation.

By the above calculation, the rate of production of trans should be 10^7 times as great in benzene as in cumene, if only the free radical mechanism were operative. Therefore the enhanced production of cis-stilbene in cumene with chloranil and 9,10-dibromoanthracene must be attributable to the fact that when the radical process is quenched, the photochemical process is relatively more efficient. With those sensitizers which show less change in the rate of formation of cis in the different solvents, the lack of quenching can be attributed to attack by cumyl radicals, which are formed by the destruction of the semiquinones.

By making several estimates for certain rate constants, it is possible to approximate the relative importances of the free radical and photochemical processes. The following equations describe the sensitized process.

$$ {}^3Q + t \xrightarrow{k_{12}} Q + {}^3t \qquad (4.11.12) $$

$$ {}^3Q + c \xrightarrow{k_{13}} Q + p \qquad (4.11.13) $$

$$ {}^3t \xrightarrow{k_{14}} p \qquad (4.11.14) $$

$$ p \xrightarrow{k_{15}} {}^3t \qquad (4.11.15) $$

$$ p \xrightarrow{k_{16}} t \qquad (4.11.16) $$

$$ p \xrightarrow{k_{17}} c \qquad (4.11.17) $$

Reversible energy transfer between <u>trans</u> and the sensitizer was disregarded for simplicity but is perhaps operative for a few of the sensitizers studied.

$$ \varphi_{t\ \text{sensit.}} = \frac{1}{E} \frac{k_3\, k_{16}[{}^1Q]}{k_{16} + k_{17}} \qquad (4.17) $$

$$ \frac{\varphi_t(\text{radical})}{\varphi_t(\text{sensitization})} = \frac{k_6(k_{16} + k_{17})}{k_3\, k_{16}(k_6 + k_7)} \left(k_4[t\text{-}S] + k_5[c\text{-}S]\sqrt{\frac{k_1}{k_9}\frac{[IH]}{[{}^1Q]}}\right) \qquad (4.18) $$

$k_{16} \simeq k_{17} \simeq 10^{10}$ (since the phantom is too short lived to be quenched but lives long enough to establish equilibrium with ${}^3t$)

$$ k_6 \simeq k_7 $$

$k_4 \simeq k_5 \sim 10^6$ (estimated value)

Using the above numbers in Equation 4.18 predicts that in benzene the radical process should be more than 100 times as effective as the energy transfer process, but of course this value is as uncertain as k_4 and k_5.

The rates are almost certainly of comparable magnitude, however.

For the methyl substituted stilbenes the above description is incomplete in that it does not include the possibility that the primary hydrogen abstraction can occur using hydrogen atoms supplied by the substrate itself. The following scheme would appear to present a reasonably complete picture of this hydrogen abstraction process.

$$Q + h\nu \xrightarrow{k_1} {}^1S \qquad (4.19.1)$$

$${}^1Q + \text{t-BH} \xrightarrow{k_2} QH\cdot + B\cdot \qquad (4.19.2)$$

$${}^1Q + \text{c-BH} \xrightarrow{k_3} QH\cdot + B\cdot \qquad (4.19.3)$$

$${}^1Q + BH \xrightarrow{k_4} QH\cdot + B\cdot \qquad (4.19.4)$$

$${}^1Q + CH \xrightarrow{k_5} QH\cdot + C\cdot \qquad (4.19.5)$$

$$B\cdot + CH \xrightarrow{k_6} \text{t-BH} + C\cdot \qquad (4.19.6)$$

$$B\cdot + CH \xrightarrow{k_7} \text{c-BH} + C\cdot \qquad (4.19.7)$$

$$B\cdot + CH \xrightarrow{k_8} BH + C\cdot \qquad (4.19.8)$$

$$B\cdot + QH\cdot \xrightarrow{k_9} \text{t-BH} + Q \qquad (4.19.9)$$

$$B\cdot + QH\cdot \xrightarrow{k_{10}} \text{c-BH} + Q \qquad (4.19.10)$$

$$B\cdot + QH\cdot \xrightarrow{k_{11}} BH + Q \qquad (4.19.11)$$

$$B\cdot + \text{t-BH} \xrightarrow{k_{12}} \text{c-BH} + B\cdot \qquad (4.19.12)$$

$$B\cdot + \text{t-BH} \xrightarrow{k_{13}} BH + B\cdot \qquad (4.19.13)$$

$$B\cdot + \text{c-BH} \xrightarrow{k_{14}} \text{t-BH} + B\cdot \qquad (4.19.14)$$

$$B\cdot + \text{c-BH} \xrightarrow{k_{15}} BH + B\cdot \qquad (4.19.15)$$

$$B\cdot + BH \xrightarrow{k_{16}} \text{t-BH} + B\cdot \qquad (4.19.16)$$

$$B\cdot + BH \xrightarrow{k_{17}} c\text{-}BH + B\cdot \qquad (4.19.17)$$

$$2C\cdot \xrightarrow{k_{18}} C_2 \qquad (4.19.18)$$

$$2C\cdot \xrightarrow{k_{19}} M + CH \qquad (4.19.19)$$

$$2QH\cdot \xrightarrow{k_{20}} D \qquad (4.19.20)$$

$$QH\cdot + CH \xrightarrow{k_{21}} QH_2 + C\cdot \qquad (4.19.21)$$

$$QH\cdot + IH \xrightarrow{k_{22}} QH_2 + I\cdot \qquad (4.19.22)$$

$$B\cdot + IH \xrightarrow{k_{23}} t\text{-}BH + I\cdot \qquad (4.19.23)$$

$$B\cdot + IH \xrightarrow{k_{24}} c\text{-}BH + I\cdot \qquad (4.19.24)$$

$$B\cdot + IH \xrightarrow{k_{25}} BH + I\cdot \qquad (4.19.25)$$

$$2B\cdot \xrightarrow{k_{26}} B_2 \qquad (4.19.26)$$

t-BH and c-BH are the methyl substituted stilbenes and BH is the corresponding structural isomer of the substituted stilbene. The sources of hydrogen atoms in the above are cumene, 2,3-diphenylbutene-1,2 or 1,2- and 2,3-diphenylpropene, the semiquinone radical, impurity, or hydroquinone, which can be discounted due to its low solubility. Clearly reactions 5,6,7,8,18,19,20 can be discounted in benzene and 9,10,11,21,22,23, 24,25,26 can be discounted in cumene. Quantitative description of the above system is considerably more complex than was the case with stilbene, where the isomerizable substrate does not itself contain an abstractable hydrogen atom, because of the innumerable second-order terms involved. These make solution for the quantum yields in terms of a few easily estimable parameters essentially impossible. Simply by inspection it is again clear that the rates of both cis-trans isomerization and the con-

comitant isomerization to the structural isomers would be suppressed in cumene, although it is difficult to estimate by how much. This suppression, both of rate and extent of product formation was observed experimentally in samples irradiated for equal times, as can be seen from Tables 24, 27 and 28. It would be of interest to study the dependence of the rates of isomerization and product formation as a function of the concentrations of substituted stilbene and sensitizer with several of these sensitizers. The balance between hydrogen abstraction and addition-elimination should be strongly influenced by these parameters. Again, with this mechanism, the purely photochemical process would be expected to be more important in cumene.

There are two important features of the data, which, while they have been mentioned previously, deserve some further comment. As can be seen from scrutiny of Tables 24, 27 and 28, the photostationary states to which these systems tend to converge are only in a few cases close to thermodynamic equilibrium mixtures (stilbene 99+% trans, 2,3-diphenylbutene-2 55-60% trans) (58,59). This can be explained only if the radical attack or expulsion is in some way photolytically influenced. Since these pseudostationary states are not close to thermodynamic equilibrium, and some type of free radical reaction is clearly implicated, there is a strong suggestion that there must be a photochemical influence on some step in the chain mechanisms which were written. This photochemical intrusion on the thermodynamic process is, in a sense, polyphotonic, as absorption of one photon initiates the chain process and another opens the way to further photochemical steps.

It is highly unlikely that the attacking radical retains any of its excitation energy, so a probable specific example of a polyphotonic process would be a requirement that absorption of a second photon precede the collapse of the addition complex between stilbene and radical. This, or any alternative proposal could occur either by direct absorption of some transient species or by energy transfer from some excited component of the system. Any such polyphotonic reactions would necessarily be affected both by the intensity and the wavelength of the exciting light. Such a wavelength dependence is clearly noted with stilbene and benzoquinone (table 24) and a slight effect exists with stilbene and duroquinone.

The other effect cannot be accounted for by any combination of photochemical, radical attack, or adduct-forming processes. This is the frequently observed (at least in substituted stilbene systems) time variation of isomer ratios through a maximum of cis. The cis-rich mixtures formed early in the reaction are probably genuine combinations of the above listed reactions. However, the long term trans-rich photostationary states observed with 2,3-diphenylbutene-2 are almost certainly the result of slow production of some product of the free radical reactions, or some other light induced chemical reaction such as adduct formation, which prevents continuing isomerization by either the radical or the triplet state of the original sensitizer by preferential absorption of the exciting light. Judging by the photostationary state reached with 2,3-diphenylbutene-2 and all of the various quinone-type sensitizers, the triplet energy of this compound must be around 54-56 k. cals. Since both stilbene and sensitizer are destroyed by prolonged

irradiation, a wide variety of structures for the new sensitizer can be imagined.

Although the above discussion has been centered mostly about the quinone-type sensitizers, there are no elements of it which cannot with very slight modifications be applied also to either the halogen-containing compounds (as has been mentioned) or to the diketone sensitizers. The diketones do, however, present some additional problems. The fact that under irradiation some isomerization occurs to 2,3-diphenylpropene or 2,3-diphenylbutene-1 indicates that hydrogen abstraction does operate to some extent in these systems. However, the lack of important differences in the relative rates of isomerization in the different solvents probably indicates that hydrogen abstraction or addition elimination is not a major effect. It is certain, from the appearance of several side products with some of these sensitizers, that several chemical or photochemical processes are occurring, probably including adduct formation such as that reported by Bohning and Weiss. This system, which is considerably cleaner chemically than that of the quinones and halogen-containing compounds, could perhaps be completely analyzed by more extensive study. Electron paramagnetic resonance studies coupled with product analysis would be most effective.

In summary of the above section, it can be said definitely that free radicals are formed which have lifetimes long enough to effect chemical changes in the stilbene systems. The occurrence of structural isomerization and the semiquantitative effects of solvent on cis-trans isomerization point to the conclusion that these radicals are directly involved in the photoisomerization process. In view of the type of

photostationary states observed and the evidence for a wavelength effect on the stationary state, it would furthermore appear that the role of these radicals is not trivially that of initiators of a chain reaction, but is that of true photochemical intermediates.

Although these enormously complex systems have not been completely characterized, it is clear that the original structured nature of the Saltiel plots must and can be explained by factors in addition to that of primary photochemical excitations. However, it is also apparent that photochemical energy is of significance to the anomalous sensitizers as well as the normal ones. It is necessary, however, that energy be used with discretion as a parameter in the case of certain classes of reactive compounds.

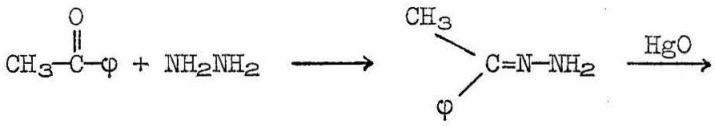
P A R T 5

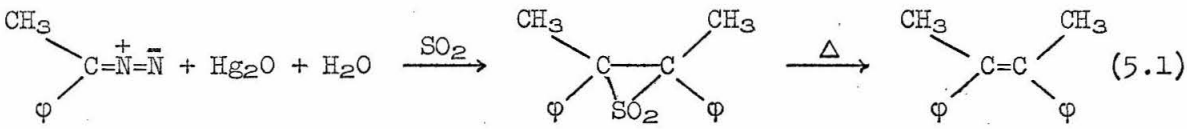
EXPERIMENTAL SECTION

Substrates

2,3-Diphenylbutene-2.--2,3-Diphenylbutene-2 was synthesized from phenylmethyl diazomethane by the method of Vargha and Kovacs (60). The procedure for synthesizing the precursors and converting them to the desired olefin is as follows: Acetophenone, reagent grade (34 moles or ~ .29 moles) and hydrazine hydrate (Matheson, Coleman and Bell 99-100%) (22 moles or ~ .59 moles) were warmed in 75 moles of absolute ethanol to ~ 60° for about 1 hour. The reaction mixture was then heated to reflux for approximately two more hours. The ethanol was then stripped off over a steam bath using a rotary evaporator and aspirator. The residue appeared as a yellow oil at room temperature, but the hydrazone crystallized out as white needles in the refrigerator. The oil was recrystallized 3 times from pentane. About 30 gms of pentane wet crystals were mixed with 55 gms of yellow mercuric oxide (Baker Analytical Reagent) and 10 gms of sodium sulfate (Baker Analytical Reagent) in 350 c.c. of 30/60 petroleum ether. For some preparations diethyl ether was used as the solvent but is not recommended as it reduces the yield to ~ 0% 2,3-diphenylbutene-2 in favor of acetophenone azine. The solution was stirred vigorously for ~ 15 min. The intensely ruby red solution was filtered to remove inorganic salts. The filtered solution was cooled to 0° in an ice-water bath and sulfur dioxide was bubbled in slowly until the red color had completely disappeared. The episulfone separated out as a slightly yellowed white precipitate leaving a clear yellow supernatant. The precipitate was heated for one hour to > 100° in an oil bath to decompose the episulfone. After stripping off the solvent, this procedure was

repeated for the solution. The solid material was then dissolved in 30/60 pet ether and chromotographed on alumina until all trace of the yellow coloration (acetophenone azine) had disappeared. The chromatographed material was recrystallized at least twice from ethanol. Compound from the precipitate, m.p. 105°, was only slightly contaminated by the cis-isomer but the section from the solution contained varying, but considerably larger portions of cis. No attempt was made to isolate pure cis since such small amounts were produced. Some pure trans was isolated by successive recrystallizations.





(5.1)

This method is not highly recommended for its dependability. Frequently, for no obvious, or subtly obvious, reason the greatest portion of the reagents convert themselves spontaneously to acetophenone azine.

cis- and trans-1,2-Diphenylpropene.--Both cis- and trans-1,2-diphenylpropene were generously supplied by Dr. D. J. Cram and were used without further purification.

trans-Stilbene.--trans-Stilbene was supplied by D. H. Valentine. It was Matheson, Coleman and Bell scintillation grade twice recrystallized from ethanol and sublimed under vacuum at about 80° (1 mm), m.p. 125.6-125.8.

Solvents

Benzene.--Benzene (Matheson, Coleman and Bell or Malinkrodt Reagent Grade) was shaken with sulfuric acid until yellow discoloration ceased, washed with distilled water, saturated sodium bicarbonate solution, distilled water, dried over magnesium sulfate, then distilled from sodium wire or phosphorous pentoxide. The middle fraction was collected, boiling point 80°. If discoloration of phosphorous pentoxide occurred, the batch was redistilled from fresh phosphorous pentoxide. For the free radical experiments the procedure was the same, except that before distillation the benzene was irradiated for one week in the presence of chloranil. The irradiated product was chromatographed on alumina, then distilled.

Cumene.--Cumene (Eastman White Label) was treated like benzene except that distillation from sodium wire was done under a reduced pressure of nitrogen. The storage container was flushed with dry nitrogen before storing. The batch was redistilled before each use.

Methylcyclohexane.--Methylcyclohexane (Matheson, Coleman and Bell Reagent Grade) was purified by washing with sulfuric acid, water, saturated sodium bicarbonate, water, and distillation from sodium wire.

Isopentane.--Isopentane (Phillips 66 Pure Grade) was purified in the same manner as methylcyclohexane, above.

Ethyl benzoate.--Ethyl benzoate (Matheson, Coleman and Bell Reagent Grade) was distilled under reduced pressure.

Ethyl iodide.--Ethyl iodide (Matheson, Coleman and Bell Reagent Grade) was distilled in the dark from mercury immediately before using, b.p. 71°.

Sensitizers

9,10-Dibromoanthracene.--9,10-Dibromoanthracene was supplied by Dr. Jack Saltiel for the sensitized isomerization experiments. For the free radical experiments it was supplied by Mr. George Vesley. It had been repeatedly recrystallized and vacuum sublimed, m.p. 228.6-229°.

Anthracene.--Anthracene (Matheson, Coleman and Bell, Blue Violet Fluorescence) was used without further purification.

Eosin.--Eosin (student preparation) was recrystallized by Dr. John Fox and Lelia Coyne from acetone.

Benzanthrone.--Benzanthrone was chromatographed on alumina using benzene as eluent. The chromatographed material was concentrated to dryness and recrystallized from methanol, m.p. 173.5-173.8°.

1,2-Benzanthracene.--1,2-Benzanthracene was supplied by Dr. Jack Saltiel. It was Eastman White Label and had been dissolved in benzene and passed through a rosite column. The benzene was evaporated and the yellow solid was recrystallized from ethanol. The yellow crystals were recrystallized from ethanol, then dissolved in benzene and chromatographed on alumina, using benzene as eluent. Upon concentration and cooling, white crystals were obtained from the eluent, m.p. 158.9-159.0°.

Acridine.--Acridine (Eastman Kodak Practical Grade) which had been dissolved in diethyl ether and chromatographed on rosite, concentrated and precipitated out by 30/60 ligroin to produce yellow needles, m.p. 110.0°, was obtained from Dr. Jack Saltiel.

Pyrene.--Pyrene was supplied by Dr. Jack Saltiel. It was Matheson, Coleman and Bell, Practical Grade which had been dissolved in benzene and chromatographed on rosite. The eluent was concentrated to dryness and the residue was recrystallized from ethanol. White crystals were obtained which melted at 149.0-149.2°.

p-Benzoquinone.--p-Benzoquinone (Matheson, Coleman and Bell, Practical Grade) was sublimed 2-3 times immediately prior to use.

Duroquinone.--Duroquinone (Aldrich Research Grade) was sublimed at reduced pressure 2-3 times before use.

1,2,5,6-Dibenzanthracene.--1,2,5,6-Dibenzanthracene (Eastman Kodak White Label) was obtained from Dr. H. P. Waits following purification by recrystallization from acetic acid and vacuum sublimation.

9-Fluorenone.--9-Fluorenone was zone refined under a reduced pressure of nitrogen by Dr. W. Herckstroeter, m.p. 83.8-84.0°.

Benzil.--Benzil was supplied by Dr. Jack Saltiel. It was Matheson, Coleman and Bell, Reagent Grade which had been recrystallized from 85/100 ligroin, hot stage m.p. 96.2-96.6°. The free radical work was done with benzil purified by Mr. Stephen Elliot.

Coronene.--Coronene (Aldrich Research Grade) was treated with norite and recrystallized from ethanol. Its u.v. spectrum was compared to the literature spectrum. Also it showed only the proper phosphorescence spectrum.

α-Naphthaldehyde.--α-Naphthaldehyde was supplied by Dr. Jack Saltiel. It was Eastman White Label which was distilled twice at 1 mm pressure. The fraction boiling at 103-104° was collected and stored in a refrigerator until used.

Mesityl 2-naphthyl ketone.--This compound was obtained from the University of Illinois Research Stockroom and was used as received.

Chrysene.--Chrysene was chromatographed on alumina and recrystallized from benzene, m.p. 247-247.5° uncorr.

1-Naphthyl phenyl ketone.--1-Naphthyl phenyl ketone was obtained from Dr. Jack Saltiel. It had been recrystallized from benzene, hot stage m.p. 76.4-77.0°.

2-Acetonaphthone.--2-Acetonaphthone was obtained from Dr. Jack Saltiel. It was Eastman White Label and had been recrystallized from 85/100 ligroin, hot stage m.p. 54.1-54.6°.

2-Naphthyl phenyl ketone.--2-Naphthyl phenyl ketone was obtained from Dr. Jack Saltiel. It was K.&K., Practical Grade which had been chromatographed on alumina with n-pentane and benzene as eluents. The n-pentane was discarded. The benzene solution was passed through a rosite column and the eluent was concentrated and cooled. The ketone

crystallized out in white crystals, hot stage m.p. 83.5-84.3°.

4-Acetylbiphenyl.--4-Acetylbiphenyl was obtained from Dr. Angelo Lamola. Aldrich Research Grade was chromatographed on alumina with benzene as eluent, treated with carbon black in methanol and recrystallized from methanol.

2-Acetylfluorene.--2-Acetylfluorene was obtained from Dr. Angelo A. Lamola. It was Aldrich Research Grade which had been chromatographed on alumina using benzene for an eluent. It was then recrystallized from methanol, m.p. 132.0-133.0°.

Flavone.--Flavone (Aldrich Research Grade) was used without further purification, m.p. 97.0°.

9,10-Anthraquinone.--9,10-Anthraquinone was supplied by Dr. Jack Saltiel. It was Eastman Kodak, Sublimed which had been recrystallized by Dr. C. A. Stout, m.p. in sealed tube 285.5°.

Thioxanthone.--Thioxanthone was obtained from Dr. Jack Saltiel. It was purified using the procedure described for 4-acetylbiphenyl. Its m.p. was 209.0°.

Triphenylene.--Several procedures were used to purify triphenylene. One sample was obtained zone-refined from James Hinton, Ph.D. and was used without further purification. Another was Aldrich Research Grade which was zone-refined by Dr. Charles De Boer, m.p. 198-199°. A third sample was vacuum sublimed by Dr. John Fox. Starting material in this case was also Aldrich Research Grade. Most of the work done, how-

ever, was performed with triphenylene (Aldrich Research Grade) which was either treated with norite in ethanol, or chromatographed on alumina with benzene as eluent and recrystallized twice from ethanol to yield very fine, fluffy white needles, m.p. 198-198.5°.

2,4,6-Trimethyl,4'-methoxybenzophenone.--This compound was obtained from the Research Stockroom of the University of Illinois and was used as received.

Benzophenone.--Benzophenone was supplied by Dr. D. H. Valentine. It was Matheson, Coleman and Bell Reagent Grade which had been recrystallized 3 times from ethanol, m.p. 45.8-46.0°.

2,4,6-Triisopropylbenzophenone.--2,4,6-Triisopropylbenzophenone was obtained from the Research Stockroom of the University of Illinois and was used as received.

Triphenylmethyl phenyl ketone.--Triphenylmethyl phenyl ketone was obtained from the Research Stockroom of the University of Illinois and was used as received.

p-Methoxyphenyl-2,3,5,6-tetramethylphenyl ketone.--This compound was obtained from the Research Stockroom of the University of Illinois and was used as received.

Benzaldehyde.--Benzaldehyde was obtained from Dr. William Hardham. It was Matheson, Coleman and Bell, Reagent Grade, which had been distilled twice, the second time through a spinning band column, b.p. 65° at 25 mm.

1,3,5-Triacetylbenzene.--1,3,5-Triacetylbenzene was supplied by Dr. Angelo Lamola.

Xanthone.--Xanthone was supplied by Dr. Jack Saltiel who chromatographed it on a combination rosite and alumina column, eluting with benzene. After concentration, the eluent was cooled yielding white crystals, hot stage m.p. 171.9-172.2°.

Propiophenone.--Propiophenone was obtained from Dr. William Hardham. It was Matheson, Coleman Reagent Grade which had been recrystallized from ligroin at -5° and distilled at 0.5 mm through a vigreaux column; the fraction collected for use boiled at 63-64°.

Michler's ketone.--Michler's ketone (Eastman Kodak Practical Grade) was recrystallized twice from methanol and washed with 30/60 ligroin by Dr. N. J. Turro, m.p. 171.0-171.5°.

Biacetyl.--Biacetyl (Eastman White Label) was distilled immediately before use. The middle fraction, boiling at 78° was collected.

β-Naphthil.--β-Naphthil was prepared and purified by Dr. Jack Saltiel.

Azulene.--Azulene (Aldrich Research Grade) was sublimed twice at reduced pressure immediately before using.

Chloranil.--Chloranil (Matheson, Coleman and Bell, Practical Grade) was purified by recrystallization from acetone and benzene and subsequently was sublimed twice at reduced pressure.

1,4-Naphthoquinone.--1,4-Napthoquinone (Matheson, Coleman and Bell, Reagent Grade) was dissolved in ethanol and passed through a rosite column and was then sublimed twice.

p-Hydroquinone.--p-Hydroquinone (Matheson, Coleman and Bell, Reagent Grade) was recrystallized twice from distilled water.

p-Deuteroquinone.--p-Deuteroquinone was recrystallized twice from water and twice from deuterium oxide. N.M.R. analysis showed that 82% deuteration of the OH groups had occurred and there was no ring deuteration.

Methyl-p-benzoquinone.--Methyl-p-benzoquinone (Eastman Kodak, Practical Grade) was passed through a rosite column and sublimed twice.

Methyl-p-hydroquinone.--Methyl-p-hydroquinone (Eastman White Label) was used without further purification.

Phenyl-p-benzoquinone.--Phenyl-p-benzoquinone (Eastman White Label) was used without further purification.

m-Xylene.--m-Xylene (Matheson, Coleman and Bell, Reagent Grade) was used without further purification.

Tetraphenyl tin.--Tetraphenyl tin (Aldrich Research Grade) was used without further purification.

Tetraphenyl lead.--Tetraphenyl lead (Aldrich Research Grade) was used without further purification.

Preparation of Samples

Three mls. of solutions upon which photostationary measurements were to be made were placed in constricted 13 mm pyrex test tubes which had been washed thoroughly with labtone and repeatedly rinsed with distilled water and dried several hours at 110°. They were evacuated by 4 freeze-pump-thaw cycles to a pressure of $\sim 5 \times 10^{-4}$ mm and were then sealed off. Solutions ($1\frac{1}{2}$ mls.) for the triphenylene quenching measurements and all of the free radical experiments were placed in 7 mm. constricted tubes with ground glass joints and grease traps which had been washed thoroughly before sealing and dried in the annealing oven after sealing on to the joints. They were evacuated on the same system as were the photostationary state tubes.

Samples for the e.p.r. experiments were placed in 4-5 mm diameter quartz test tubes with grease traps and evacuated to $\sim 5 \times 10^{-7}$ mm by 4 freeze-pump-thaw cycles.

Irradiation of samples.--Irradiation took place in the frequently described merry-go-round, or by taping the samples to a quartz immersion well in cases where duplication of conditions of light absorption was unnecessary. Either a pyrex or a uranium glass filter was used. The uranium glass filter was a sleeve of 0.25 cm. thickness which transmits only those wavelengths > 3400 Å. The pyrex sleeve was 0.25 cm. thick and transmits ~ 10% at 2800 Å, 40% at 3100 Å, 75% at 3340 Å, and > 90% at 3660 Å. Samples were cooled in a water bath during irradiation. A Hanovia 450 watt medium pressure mercury lamp was used for all irradiations.

Analysis

Analysis of samples was done on either a Loenco 15 B thermal v.p.c. or a Loenco Model 160 unit which has dual flame ionization detectors. A column of 10 feet of 10 or 20% Apieson L on Chromosorb W (HMDS treated) was used for separation of the various stilbene isomers. Temperatures of ~ 200-220° were needed for 2,3-diphenylbutene-2, 220-240° for 2,3-diphenylpropene and stilbene. The injector block temperature was maintained at ~ 260°. No isomerization of any of the stilbenes occurred in the injector block or on the column.

Identical results were obtained by use of the integrator on the recorder and by cutting out the peaks and weighing them. The ± values listed in the tables represent average deviations of 2 to 5 measured values (usually 3).

Absorption and Emission Spectra

All spectrophotometric measurements were made on a Cary Model 14 Spectrophotometer. All emission measurements, with the exception of the triphenylene quenching experiments described in Table 14, were done by irradiating the samples with an AH6 Mercury arc at right angles to a scanning monochromator (Jarrell-Ash 1/2 meter). The signal was picked up by an EMI 9558B phototube, amplified and presented on a strip chart recorder. The experiments in Table 14 were done with an Aminco-Bowman Spectrophotofluorometer.

The e.p.r. work was described thoroughly in a research report by D. E. Wood.

APPENDIX I

SCHEME II. SIMPLIFIED SINGLET MECHANISM

This scheme ignores reversibility of complex formation on the basis of lack of temperature effects on the photostationary state. Quenching of triphenylene by stilbene is ignored on the basis of the fluorescence quenching experiments.

The system of equations for this and all subsequent schemes was solved by application of the steady-state condition for excited states and the photostationary state condition,

$$\frac{d}{dt}[t] = -\frac{d}{dt}[c] = 0$$

$$[^1S] = [S]\,\frac{(k_1 + k_5[^1c] + k_4[^1t])}{k_{14}}$$

$$[^1t] = \frac{k_2[t]}{(k_4 + k_6)[S] + k_{12}}$$

$$[^1c] = \frac{k_3[c]}{(k_5 + k_7)[S] + k_{13}}$$

$$[^1St] = \frac{k_6[^1t][S]}{k_8 + k_9} = \frac{k_2k_6[t][S]}{(k_8 + k_9)[(k_4 + k_6)[S] + k_{12}]}$$

$$[^1Sc] = \frac{k_7[^1c][S]}{k_{10} + k_{11}} = \frac{k_3k_7[c][S]}{(k_{10} + k_{11})[(k_5 + k_7)[S] + k_{13}]}$$

$$\frac{d}{dt}[t] = -k_2[t] + k_4[^1t][S] + k_8[^1St] + k_{11}[^1Sc] + k_{12}[^1t] = 0$$

$$\frac{d}{dt}[c] = -k_3[c] + k_5[^1c][S] - k_9[^1St] - k_{10}[^1Sc] - k_{13}[^1c] = 0$$

a) Eliminate [^{1}St] between the above expressions for the derivatives of cis and trans.

b) Substitute in the expressions for excited state concentrations in terms of ground-state concentrations as determined from the steady-state conditions.

c) Combine and group terms in [cis] and [trans] to obtain Equation 3.5.15.

SCHEME III. SIMPLIFIED SINGLET MECHANISM INCORPORATING A CONCENTRATION DEPENDENCE

$$\frac{d}{dt}[^1S] = k_1[S] + k_4[^1t][S] + k_5[^1c][S] - k_{14}[^1S] = 0 \quad (1)$$

$$\frac{d}{dt}[^1t] = k_2[t] - k_4[^1t][S] - k_6[S][^1t] - k_{12}[^1t] = 0 \quad (2)$$

$$\frac{d}{dt}[^1c] = k_3[c] - k_5[^1c][S] - k_7[S][^1c] - k_{13}[^1c] = 0 \quad (3)$$

$$\frac{d}{dt}[^1St] = k_6[S][^1t] - (k_8 + k_9)[^1St] - k_{15}[^1St][c] = 0 \quad (4)$$

$$\frac{d}{dt}[^1Sc] = k_7[S][^1c] - (k_{10} + k_{11})[^1Sc] + k_{15}[^1St][c] = 0 \quad (5)$$

$$\frac{d}{dt}[t] = -k_2[t] + k_4[^1t][S] + k_8[^1St] + k_{11}[^1Sc] + k_{12}[^1t] + k_{15}[^1St][c] = 0 \quad (6)$$

$$\frac{d}{dt}[c] = -k_3[c] + k_5[^1c][S] + k_9[^1St] + k_{10}[^1Sc] + k_{13}[^1c] - k_{15}[^1St][c] = 0 \quad (7)$$

a) Add 2 and 6 to give 8.

b) Add 3 and 7 to give 9.

c) Add 8 and 9.

d) Substitute in excited-state concentrations in terms of ground-state concentrations from steady-state conditions.

e) Collect terms in [cis] and [trans]

f) Let $(k_{10} + k_{11})k_2k_6k_{15} = A$

$k_2\, k_6\, k_{15}^2 = B$

$(k_8 + k_9)k_3k_7k_{15} = D$

$k_3\, k_7\, k_{15}^2 = E$

T = total stilbene concentration to obtain Equation 3.6

SCHEME IV. SIMPLIFIED TRIPLET MECHANISM

$$\frac{d}{dt}[^1S] = k_1[S] - k_2[^1S] \quad (1)$$

$$\frac{d}{dt}[^3S] = k_2[^1S] - k_7[^3S][t] - k_8[^3S][c] \quad (2)$$

$$\frac{d}{dt}[^1t] = k_3[t] - k_4[^1t] - k_{18}[^1t] \quad (3)$$

$$\frac{d}{dt}[^1c] = k_5[c] - k_6[^1c] - k_{19}[^1c] \quad (4)$$

$$\frac{d}{dt}[^3t] = k_4[^1t] - k_9[^3t] \quad (5)$$

$$\frac{d}{dt}[^3c] = k_6[^1c] - k_{10}[^3c] \quad (6)$$

$$\frac{d}{dt}[^3St] = k_7[^3S][t] - (k_{13} + k_{14})[^3St] - k_{17}[^3St][c] \quad (7)$$

$$\frac{d}{dt}[^3Sc] = k_8[^3S][c] - (k_{15} + k_{16})[^3Sc] + k_{17}[\ St][c] \quad (8)$$

$$\frac{d}{dt}[p] = k_9[^3t] + k_{10}[^3c] - k_{11}[p] - k_{12}[p] + k_{14}[^3St] + k_{16}[^3Sc] \quad (9)$$

$$\frac{d}{dt}[t] = -k_3[t] - k_7[^3S][t] + k_{11}[p] + k_{13}[^3St] + k_{17}[^3S][c] + k_{18}[^1t] \quad (10)$$

$$\frac{d}{dt}[c] = -k_5[t] - k_8[^3S][c] + k_{12}[p] + k_{15}[^3Sc] - k_{17}[^3St][c] + k_{19}[^1c] \quad (11)$$

a) Set all derivatives equal to 0.

b) Add 7 and 10.

c) Add 8 and 11.

d) Eliminate [p] between 12 and 13.

e) Substitute in excited state concentrations.

f) Collect terms to obtain an equation in the form

$$A[c]^4 + (BT+D)[c]^3 + (ET^2 + FT + G)[c]^2 + (HT+J)[c] + (KT^2+LT) = 0$$

where T is the total stilbene concentration

SCHEME V. TRIPLET COMPLEX MODIFIED FOR SIMPLICITY

$$\frac{d}{dt}[^1S] = k_1[S] - k_{12}[^1S] \quad (1)$$

$$\frac{d}{dt}[^3S] = k_2[^1S] - k_7[^3S][t] - k_8[^3S][c] \quad (2)$$

$$\frac{d}{dt}[^1t] = k_3[t] - k_4[^1t] - k_{18}[^1t] \quad (3)$$

$$\frac{d}{dt}[^1c] = k_5[c] - k_6[^1c] - k_{19}[^1c] \quad (4)$$

$$\frac{d}{dt}[^3t] = k_4[^1t] - k_9[^3t][S] \quad (5)$$

$$\frac{d}{dt}[^3c] = k_6[^1c] - k_{10}[^3c][S] \quad (6)$$

$$\frac{d}{dt}[^3St] = k_7[^3S][t] + k_9[^3t][S] - (k_{11} + k_{12})[^3St] - k_{17}[^3St][c] \quad (7)$$

$$\frac{d}{dt}[^3Sc] = k_8[^3S][c] + k_{10}[^3c][S] - (k_{13} + k_{14})[^3Sc] + k_{17}[^3St][c] \quad (8)$$

$$\frac{d}{dt}[p] = k_{12}[^3St] + k_{14}[^3Sc] - (k_{15} + k_{16})[p] \quad (9)$$

$$\frac{d}{dt}[t] = -k_3[t] + k_{11}[^3St] + k_{15}[p] + k_{17}[^3St][c] + k_{18}[^1t] - k_7[^3S][t] \quad (10)$$

$$\frac{d}{dt}[c] = -k_5[c] - k_8[^3S][c] + k_{13}[^3Sc] + k_{16}[p] - k_{17}[^3St][c] + k_{19}[^1c] \quad (11)$$

a) Add 7 and 10 to give 12.

b) Add 8 and 11 to give 13.

c) Eliminate [p] between 12 and 13.

d) Substitute in the excited-state concentrations in terms of ground-state concentrations from steady-state conditions.

e) Let $\dfrac{k_3\, k_4\, k_7\, k_{12}\, k_{16}}{k_4 + k_{18}} = A$

$$\frac{k_5\, k_6\, k_7\, k_{14}\, k_{15}}{k_6 + k_{19}} - \frac{k_3\, k_4\, k_8\, k_{12}\, k_{16}}{k_4 + k_{18}} = B$$

$$\frac{k_5\, k_6\, k_8\, k_{14}\, k_{15}}{k_6 + k_{19}} = D$$

$$k_1\, k_7\, k_{12}\, k_{16}\, [S] = a(S)$$

$$k_1\, k_8\, k_{14}\, k_{15}\, [S] = b(S)$$

$$[t] = \frac{[T(2D-2A-B) + a(S) + b(S) + \sqrt{\begin{matrix}[T(2A-2D+B) - a(S) + b(S)]^2 \\ -4(D-A-B)[(D-A)T^2 + b(S)T\end{matrix}}}{2(D-A-B)}$$

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PROPOSITION 1

It is suggested that the techniques of chemical spectroscopy be used as a probe in the study of the efficiency of formation and the energy of triplet excimers.

* * * * * *

It is a frequently observed phenomenon that excimer fluorescence of aromatic hydrocarbons is acutely more subject to oxygen quenching than is the monomer fluorescence from the same aromatic hydrocarbons (1,2). More significantly, Ferguson (3) has reported that in studies of mono- and dimesohalo- derivatives of anthracene that the presence of these heavy atom substituents causes a variation in excimer fluorescence yield which is proportional both to the number of heavy atom substituents and to their molecular weight. In explanation of these phenomena, it was suggested that both the oxygen and the heavy atom substituent effects reflect an increase in radiationless transition probabilities to some nearby triplet state of the excited complex. It would be expected that from here, radiationless decay to the ground state would be quite rapid. In fact, phosphorescence from triplet excimers has only rarely been seen and then only at very low temperatures (4). Therefore, experimental verification of the existence of triplet excimers is difficult and the means for studying their stabilization energies and the efficiency of formation from the singlet excimer have been for the most part nonexistent.

It is therefore proposed that the techniques of chemical spectroscopy be employed to monitor production of triplet excimers. Yields and photostationary states of cis-trans isomerization of heavy atom substituted stilbenes can be compared with the equivalent values for unsubstituted stilbenes under conditions where the sensitizer is known to produce a sizeable quantity of excimers. Further studies elucidating the relative magnitudes of the external heavy atom effect with an internal heavy atom effect could be made by comparing yields of isomerization for heavy atom substituted stilbenes, using unsubstituted sensitizers and vice versa.

Under such conditions where excimer formation predominates over intersystem crossing of the monomer, the following mechanism can be proposed for sensitization of the pure trans- isomer.

$$S + h\nu \xrightarrow{k_1} {}^1S$$

$${}^1S \xrightarrow{k_2} S \quad \text{by all 1st order processes}$$

$${}^1S + S \xrightarrow{k_3} {}^1S_2$$

$${}^1S_2 \xrightarrow{k_4} 2S \quad \text{by all 1st order processes except intersystem crossing}$$

$${}^1S_2 \xrightarrow{k_5} {}^3S_2$$

$${}^1S_2 + t \xrightarrow{k_6} {}^3S_2 + t$$

$${}^3S_2 \xrightarrow{k_7} 2S \quad \text{by all 1st order processes}$$

$${}^3S_2 + t \xrightarrow{k_8} 2S + p$$

$$p \xrightarrow{k_9} t$$

$$p \xrightarrow{k_{10}} c$$

The above scheme gives the following expression for $1/\Phi_{t\rightarrow c}$.

$$1/\Phi_{t\rightarrow c} = \left(1 + \frac{k_4}{k_5 + k_6[t]}\right)\left(1 + \frac{k_7}{k_8[t]}\right)\left(\frac{k_{10}}{k_9 + k_{10}}\right)$$

Comparison between quantum yields for sensitization by triplet excimers and isoenergetic triplet monomers will give information concerning the efficiency of production of triplet excimers. If the Saltiel plot is known for the substrate, the energy of the excimer can be obtained from the photostationary isomer ratio.

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PROPOSITION II

It is proposed that phosphorescence or triplet-triplet absorption yields for aza-aromatics and the photoenolization of a series of known photochromic ketones be restudied with specific reference to the possibility of an activation energy for the intersystem crossing from the n-π^* singlet state to the n-π^* triplet state, which is reactive in the case of the ketones.

* * * * * * *

Lim, Laposa and Yu (1) have determined that the intersystem crossing of 9, or 9,10-substituted anthracenes is an activated process. This was done by measuring the temperature dependence of the fluorescence quantum yield in concurrence with the temperature dependence of initial triplet-triplet absorption. If the following mechanism is deemed sufficient to describe the system, and k_2 is assumed to be 0 (an assumption

$$^0A + h\nu \longrightarrow {}^1A$$

$$^1A \xrightarrow{k_1} {}^0A + h\nu'$$

$$^1A \xrightarrow{k_2} {}^0A$$

$$^1A \xrightarrow{k_3} {}^3A$$

which has been frequently verified for other systems (2) and which the results of Lim's investigation also justify), Step 3 is the only process for which an activation energy might be reasonably anticipated. Thus,

$$\Phi_f = \frac{k_1}{k_1 + k_2 + k_3}$$

and

$$\frac{1}{\Phi_F} - 1 = \frac{A' e^{-\Delta H/RT}}{k_1}$$

Furthermore, the initial triplet-triplet absorbance can be expressed in the following form:

$$\frac{1}{A} - p = \frac{k}{A' e^{-\Delta H/RT}}$$

where $p = 10^3 N\ cm^3/\epsilon\ Q\ \ell$

$k = (k_1 + k_2)p$

Q = number of quanta/flash absorbed by sample

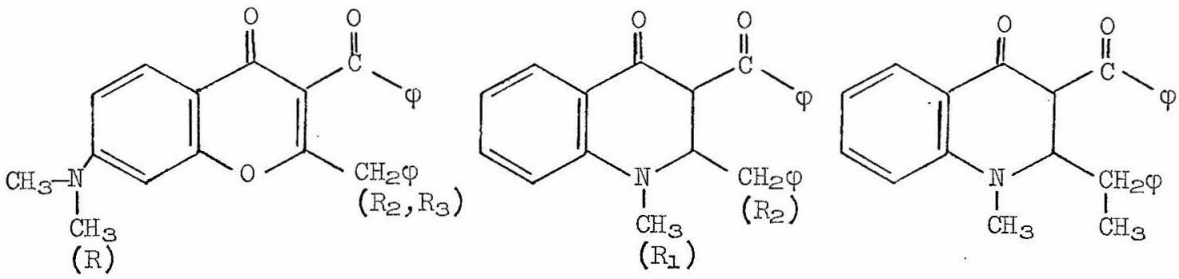
Thus there are now two independent determinations for ΔH. For 9-methylanthracene, ΔH by the first measurement was determined to be 2.4 k. cal./mole and by the second measurement was determined to be 2.3 k. cal./mole. The coincidence of the two values gives justification for having set $k_2 = 0$.

Such an activation for intersystem crossing would seem very likely to occur and would be very interesting to study in systems where there are both $n-\pi^*$ and $\pi-\pi^*$ triplet states as in nitrogen heterocyclic systems and in carbonyl compounds. For instance, El-Sayed (3) has explained the fluorescence from 9,10-diazaphenanthrene and s-tetrazine by postulating that if the $n-\pi^*$ singlet lies below the $\pi-\pi^*$ triplet, as was suggested in a calculation by El-Bayoumi and Kearns (4), then intersystem crossing could occur only through the $n-\pi^*$ triplet, which he shows to be a strongly forbidden transition. Intersystem crossing might well be activated in this system, or in other systems where intersystem

crossing can actually occur at room temperature, but might be quenched at lower temperatures.

Fortunately $n-\pi^*$ type systems can be very conveniently studied by measuring either decrease of fluorescence yield, increase of phosphorescence yield, or triplet-triplet absorption, since relative spacings of $n-\pi^*$ and $\pi-\pi^*$ levels are a function not only of molecular structure, but solvent as well. Thus temperature dependence studies as a function of solvent could be hoped to give semiquantitative information about the position of the second triplet, which is never amenable to study by phosphorescence, and only in favorable cases amenable to study by triplet-triplet absorption.

Not only is the phenomenon interesting in itself, but activated intersystem crossing may be of practical significance in explaining certain photochemical processes. Huffman, et al. (5) have studied a series of photochromic ketones, some of which turned out to be unexpectedly non-photochromic. For those compounds which were photochromic, the photochromism was shown to be attributable to photoenolization. Photoenolization has been shown in some cases to result from an $n-\pi^*$ triplet state (6). Thus, for some compounds which are neither photochromic nor otherwise indicate the occurrence of photoenolization, this could be the result of a $\pi-\pi^*$ lowest triplet state. For those non-photochromic compounds which contained heavy atom groups, it is possible that the $n-\pi^*$ triplet lifetime is so diminished by the substituents as to preclude chemical reaction. However, the following three compounds,



were photochromic at room temperature but not in a glass at 77°K, where the reverse reketonization is generally found to be inhibited. Although the authors themselves postulated an activated intersystem crossing process for certain other compounds in the series, they rejected it for these in favor of the alternative that lowering of the temperature might result in inversion of the n-π^* and π-π^* triplet energy levels. This alternative would seem to be highly inferior to the possibility of activated intersystem crossing. Of course it is possible that the enolization step is the activated process, but there are several arguments which should diminish the importance of this alternative.

1. Those compounds which do not enolize also show no phosphorescence at low temperature unless polar additives are present, indicating that the triplet state really is not efficiently populated, or that radiationless decay from the triplet is very rapid.
2. Many compounds differing only in R, R_1 and R_2 do photoenolize efficiently at low temperature. It would seem that non-hindering substituents would have only a small effect on the activation energy of enolization, whereas they could have a large effect on the spacings of energy levels in the excited ketones.
3. For the vast majority of compounds studied, if enolization proceeds at room temperature, it proceeds more efficiently

at lower temperatures. Frequently compounds enolize only at reduced temperature. This would indicate that the enolization normally has a low activation energy, whereas the reverse reketonization is activated.

Thus it is proposed that photoenolization and phosphorescence of these and related compounds be studied as a function of temperature and solvent to determine the existence of an activation effect and its dependence on excited state energy level spacings.

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PROPOSITION III

It is proposed that an intensive study be made of the low temperature radiation chemistry of substituted benzoquinones and their corresponding hydroquinones as solutes in various organic glasses. This study should elucidate the nature of various hole, hydrogen atom and electron transfer processes in photosynthesis.

* * * * * * * *

It has been definitely established that a substituted benzoquinone, plastoquinone, is intimately involved in the primary photochemical process of photosynthesis (1,2). It has not been clearly demonstrated that a quinone is implicated directly in the pigment system responsible for CO_2 reduction, but it is certain that quinones play a major role in the pigment system associated with the Hill reaction, i.e., oxygen evolution in green plants (3).

Questions concerning the necessity and nature of trapping sites, the required maximum or minimum separations for reactive components of the photosynthetic system, as well as orientation factors and the intimacy of involvement of the various accessory pigment systems are, to date, almost completely unanswered.

In an attempt to determine the oxidative and reductive capabilities of the hydroquinone-chlorophyll or quinone-chlorophyll systems, Banergee and Tollin (4) have devoted considerable effort to the liquid phase study of single electron oxidations of hydroquinone and single electron reductions of quinone by photoexcited chlorophyll and pheophytin. They have concluded that both reactions are reversible, have small

temperature coefficients and proceed through a common intermediate, the benzosemiquinone free radical. They monitored this intermediate by means of its e.p.r. spectrum. Since there is also evidence that one of the transient e.p.r. signals observed in living cells is attributable to the plastoquinone semiquinone (5) the model and perhaps some of the biologically active systems would appear to be emenable to analysis by electron paramagnetic resonance.

A good amount of information can be obtained about the trapping or scavenging properties of various organic solutes by studying the radiation chemistry of solutions of the compound of interest at low temperature in glasses of organic solvents, the low temperature radiation chemistry of which has already been established. For instance, methyl tetrahydrofuran is known to conduct electrons to a solute but to scavenge holes in the following manner,

$$C_5H_{10}O \longrightarrow C_5H_{10}O^+ + e^-$$

$$C_5H_{10}O^+ + C_5H_{10}O \longrightarrow C_5H_{10}OH^+ + C_5H_9O$$

$$\text{solute} + e^- \longrightarrow \text{solute}^-$$

whereas butyl chloride scavenges electrons irreversibly but conducts holes (6)

$$RCl \longrightarrow RCl^+ + e^-$$

$$RCl^+ + RCl \longrightarrow RCl + RCl^+ \quad \text{(resonance charge transfer)}$$

$$RCl^+ + \text{solute} \longrightarrow RCl + \text{solute}^+$$

$$RCl + e^- \longrightarrow R + Cl^-$$

The hydrocarbon 3-methylpentane conducts holes and can reversibly trap electrons. In methanol glasses some interesting additional reactions can occur (7), with the solute, S.

$$S^- + MeOH \longrightarrow SH + RO^-$$

$$e^- + CH_3OH \longrightarrow H\cdot + CH_3O^-$$

$$CH_3OH_2^+ + e^- \longrightarrow CH_3OH + H\cdot$$

Thus solute free radicals and mobile hydrogen atoms can be produced. By judicious choice of a solvent it is clear that one has available a ready source of holes, electrons or hydrogen atoms which can migrate freely to be trapped on or scavenged by, the solute.

Using hydroquinone or benzoquinone as solute can give information about the relative efficiency of formation of semiquinone by various routes from the two precursors. A few of many possibilities are listed below.

From quinone

$$Q + e^- \longrightarrow Q^- \xrightarrow{H^+} HQ \qquad \text{(methanol)}$$

$$Q + H\cdot \longrightarrow QH \qquad \text{(methanol)}$$

$$Q^+ + H\cdot \longrightarrow QH^+ \xrightarrow{e^-} QH \qquad \text{(methanol)}$$

From hydroquinone

$$H_2Q + e^- \longrightarrow HQ^- + H\cdot \xrightarrow{-e^-} HQ \qquad \text{(MTHF)}$$

$$H_2Q + H\cdot \longrightarrow QH + H_2 \qquad \text{(methanol)}$$

$$H_2Q^+ \xrightarrow{CH_3OH} HQ + CH_3OH_2^+ \qquad \text{(methanol)}$$

Average distances of migration can frequently be obtained from the concentrations of the solutes. The active species can be monitored by e.p.r. or by optical spectroscopy. Furthermore, reversible processes can be determined by activating the metastable systems by heat or light energy. After the basic behavior of the quinone system has been characterized it would be interesting to use plastoquinone in order to see whether the unsaturated center has any function as a trap for positive holes. Olefins (8) are known to serve in this capacity.

Further studies of glasses doped with porphyrins, chlorophyll itself or various accessory pigments could be made to see what the perturbing effects of these potential traps have on the basic system. Thus the model could be made to approximate the biological system more effectively. It is possible that biologically active units could themselves be studied by this technique although it might be difficult since radiation damage could not be as effectively confined to the matrix in this case.

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PROPOSITION IV

It is suggested that vitamin B_{12} be studied with respect to its biochemical activity as an oxygen transporting agent.

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The capacity of the β-complex vitamins for preventing the acute symtoms of high altitude exhaustion and the resulting illness has been repeatedly tested by hikers and mountaineers (1,2). Specifically vitamin B_{12}, cyanocobalamin, has been tested as an aid to recovery from fatigue resulting from heavy exertion by athletes at sea levels (3). However there appears to be no general acquiescence as to the mechanism for the short-term response to heavy doses of these vitamins. Although cyanocobalamin has hemopoietic functions (4), the process of generating new blood cells is a long-term (several weeks) undertaking; therefore generation of new red blood corpuscles can not explain enhanced short-term acclimatization.

Vitamin B_{12} is a cobalt (III) chelate, the ligands being the 4 pyrrole nitrogens of a porphyrin-like skeleton and the other two a nitrogen from the benziminazole group from the 5,6-dimethyl-1-α-D-ribofuranosylbenziminazole group attached to the pseudo-porphyrin and a cyanide ion which is an artifact of the isolation procedures. The structure of the vitamin has been well detailed (5). Unlike most biologically active chelates, however, the cobalt in cyanocobalimin is bound so tightly that it will not exchange even with like atoms (6).

It is interesting to note that there is a sizeable class of stably bound cobalt chelates such as the bis-salicylaldehydeimineco-

balt (II) chelates, which are capable of reversibly absorbing and desorbing oxygen, both in the ordered lattice of certain of their crystal forms and dissolved in certain solvents (7). This leads one to suspect that some of the catalytic properties of cyanocobalamin and its derivatives might be related to oxygen transport phenomena. However, the normal oxygen transporting chelates contain cobalt in the (II) oxidation state, whereas all but a few of the naturally occurring cobalamins contain cobalt (III). This discrepancy is of minor consequence, however, since it was reported that aquocobalamin (H_2O replaces CN^- as one of the ligands) also demonstrates a capacity for reversible oxygen absorption--the only trivalent cobalt complex known to possess this property (8).

From the above it seems that more work should be done on this interesting property of vitamin B_{12} in a manner specifically designed to elucidate the physiological importance of oxygen transport as it applies to execution of the various primary and secondary metabolic functions of the vitamin. The simplest physiological experiments are concerned with measuring oxygen uptake and performance under exercise of B_{12} deficient and B_{12} saturated subjects, a few of which have been done. This can give some indication as to whether the vitamin is directly involved with the respiratory process (seemingly an unlikely process) or whether excesses of the vitamin stimulate the efficiency of consumption of available oxygen. However this type of experiment gives very little in the way of detailed mechanistic information. A more easily controlled set of experiments would involve monometric measurements of oxygen consumption of the various carboxylic and amino-acids which are oxidized by vitamin B_{12} in the marine bacterium Flavobacterium sp. (9). The nature of the ligands and the central metal ion could be

systematically varied in order to maximize and minimize the reversible absorbing properties of the vitamin. Unfortunately, this type of reaction is not extremely important in the higher animals, so some work might be involved in deriving a system which would explain the marked effect of B_{12} in oxygen deprivation and in pernicious anemia therapy. It would seem reasonable to start looking for an explanation for its behavior in terms of simple oxidation reduction reactions, however, rather than involving so many studies with complex biosyntheses of nucleic acids and proteins, most of which have been very difficult to confirm reproducibly.

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PROPOSITION V

An attempt should be made to reinterpret microwave spectral data in terms of the Regge pole formulation of Schroedinger theory.

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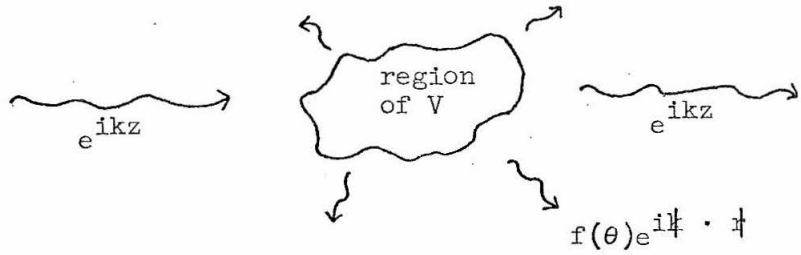
It is known that the hydrogen atom spectrum exhibits fine structure over and above that which would be predicted by the nonrelativistic Schroedinger equation. The perturbation calculation to correct for relativistic effects contains the constant $\alpha = \frac{e^2}{nc} \cong 1/137$ to various powers in various terms. This factor essentially governs the convergence of the perturbation expansion, making higher order terms increasingly less important.

Unfortunately, in the case of interactions met in high energy physics, the corresponding expansion parameter is approximately 15. Therefore a perturbation series in these problems would not tend to converge even if good zero-order Hamiltonians and wave functions could be determined. Thus a motivation has existed to reformulate Schroedinger theory in the hopes of finding a method applicable to interpretation of the data from high energy physics experiments. To date, this reformulation has had some promising advances by arguments by analogy with the nonrelativistic generalized potential scattering of Regge (1). In the years immediately following development of the theory, a few discouraging experiments were done concerning some indirect predictions of the theory. However in recent months several direct predictions have been remarkedly well verified, giving increased confidence in the application of the original theory (2).

Summary of Theory

In elementary scattering theory, an incoming plane wave interacts with a potential and is scattered. The resulting outgoing wave can be expressed as an outgoing spherical wave plus the unscattered portion of the plane wave:



In the limit as $r \to \infty$,

$$\Psi_{final} = e^{ikz} + f(\theta,E^2)e^{i\vec{k}\cdot\vec{r}}$$

where $f(\theta,E^2)$ is the scattering amplitude, i.e., the probability for scattering into $\theta + d\theta$ at energy E is $|f|^2 d\Omega$.

The analytic expression for the scattered wave can be found by application of the Schroedinger equation. However, except for simple potentials like the Coulomb potential, the resulting integral equations are very difficult to solve precisely; solution by iteration leads to the perturbation expansion, with its familiar troubles for molecular calculations. Such complications are connected with the highly approximate nature of the 0-order wave functions and their dependence on electron-electron interactions. Since high-energy physics calculations are in even worse shape because of the expansion parameter, methods have been developed (the so-called dispersion theory) to relate Re f and

Im f in a new set of integral equations (7). However, bound states of large angular momenta ruin the convergence properties of this new set of integral equations.

Regge's contribution to resolution of the prevailing confusion was to examine the nonrelativistic scattering amplitude for a given angular momentum state in the same region that led to the divergences in the relativistic case ($|\cos\theta| \gg 1$). The usual partial wave expansion of $f(\theta,E^2)$ is

$$f(\theta,E^2) = \sum_{\ell=0}^{\infty} (2\ell+1) f(\ell,E^2) P_\ell(\cos\theta)$$

and does not hold in the desired region. Regge found an integral representation for $f(\ell,E^2)$ in terms of $f(\alpha,E^2)$, where α is a complex number taking the place of ℓ, and $f(\alpha,E^2)$ is the analytic continuation of $f(\ell,E^2)$ into the complex α (angular momentum) plane. Then it was possible to formulate a representation of the old dispersion relations in which all integrals converge and the bound states, or poles of $f(\alpha,E^2)$, leading to divergences are explicitly exhibited.

The essential result is

$$f(\ell,E^2) = \sum_n \frac{\beta_n(E^2)}{\alpha_n(E^2) + \ell + 1} \frac{1}{\ell - \alpha_n(E^2)} + \text{Convergent Integrals}$$

for integer ℓ

where $\alpha_n(E^2)$ is the n^{th} pole of $f(\alpha,E^2)$;

$\beta_n(E^2)$ is its residue.

The location, number and energy dependence of these poles is not known, but must either be calculated or fitted empirically. Regge was able

to prove this representation rigorously for the Schroedinger equation when the potential was equal to a sum of Yukawa potentials,

$$V = \sum_i \frac{g_i}{r} e^{-r/r_{o_i}}$$

The r_o is the range of the potential (and is related to 1/m, where m is the mass of the "carrier" of the field), thus for the Coulomb potential, with the photon mass = 0 we obtain $r_o = \infty$ and the above expression reduces to the familiar one.

Physical Significance

a) If $\alpha_n(E^2) = \ell_o$, then this is the explicit pole of $f(\ell_o, E^2)$ and corresponds to a bound state of angular momentum

b) If $\alpha_n(E^2) = \ell_o$ + a small imaginary part, then

$$\alpha_n(E^2) = \text{Re } \alpha_n(E^2) + i \text{ Im } \alpha_n(E^2)$$
$$\approx \ell_o + (E^2 - E_o^2)\text{Re } \alpha_n'(E_o^2) + i \text{ Im } \alpha_n(E_o^2)$$

which inserted into $f(\ell, E^2)$ at the bottom of p. 150 gives

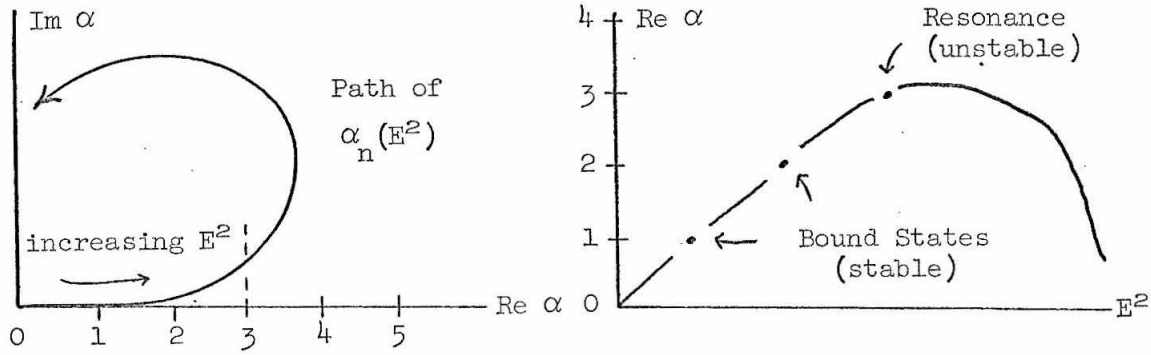
$$f(\ell_o, E^2) = \left\{ \frac{\beta(E_o^2)}{2\ell_o + 1} \quad \frac{1}{\text{Re } \alpha_n'(E_o^2)} \right\} \frac{1}{E^2 - E_o^2 + i\,\Gamma/2}$$

$$\text{with} \quad \Gamma/2 = \frac{\text{Im } \alpha_n(E_o^2)}{\text{Re } \alpha_n'(E_o^2)}$$

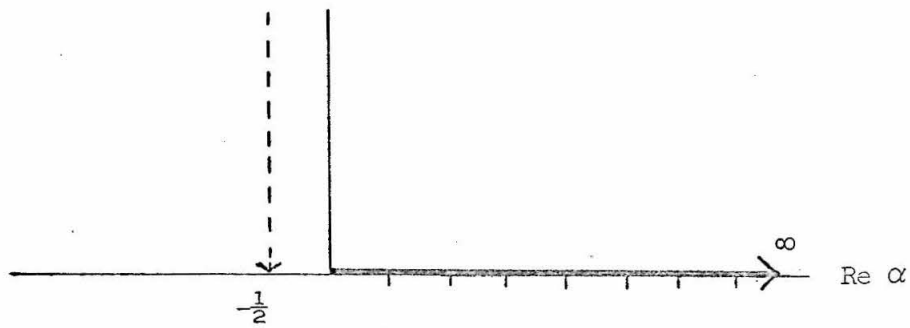
This formula is a familiar one for an almost-bound state with a natural width Γ and a lifetime proportional to $1/\Gamma$.

c) Since the poles of $f(\alpha, E^2)$ are functions of energy, they can move along trajectories in the α-plane. When the trajectory passes through ℓ_o (on the real axis), a bound state of angular momentum ℓ_o must occur in the system. If the trajectory passes over ℓ_o (in the complex

plane), an unstable state of angular momentum ℓ_o is required. The two sketches show the easy ways to represent these ideas.



d) The only common potential for which Regge trajectories have found is that for the Coulomb potential (2), which then being a very special case ($r_o = \infty$) has the weird shape shown below.



Thus an infinite number of zero width states at certain energies are predicted.

In spite of this success, the high energy physics dilemma is not yet resolved. The potentials there are not Coulomb, not even necessarily Yukawa, and thus the trajectories may not exist, or at best, some of the poles may become branch points or essential singularities (3). The attack has been to fit experimental points to Regge trajectories (4,5,6) and let the degree of success of the resulting predictions

indicate whether the theory might be valid for all potentials. Some remarkable success has been obtained in high energy physics despite the fact that when looked into more carefully the theory loses some of its elegant simplicity.

One encouraging note in the empirical attempt to generalize the Regge theory to non-Yukawa potentials has been heard from the realm of nuclear rotation studies. In the modern model of the nucleus two major types of excitation may occur (8). One of these (shell model states) has been determined to be analogous to electronic transitions in molecules. The other (collective particle model states) has an even closer analog in the vibrational-rotational states of molecules. Prof. M. Gell-Mann, in a Caltech seminar, pointed out that each sequence of nuclear rotational states seems to fit properly on a Regge trajectory. The major point of interest in this nuclear example is the generality it tends to give to the Regge hypothesis. For the nuclear rotation, the effective potential is of the same form as in the molecular case:

$$V_{eff}(r) = \frac{\hbar^2}{2\,Mr^2}\,\overline{(K-L)^2} + U(r)$$

(electronic or shell state potential)

Clearly V(r) is not a Yukawa potential, and yet the hypothesis seems to work well. Thus it is tempting to complete the cycle and borrow a result from the nuclear case, namely, that the rotational states of molecules should lie on a Regge trajectory of a similar type.

Proposal

Therefore an attempt should be made to reinterpret microwave spectral data in terms of the Regge pole formulation of Schroedinger theory. The usefulness of such a procedure is threefold:

1) Should the attempt to find a convincing fit be successful in the simple rotator states with a known non-Yukawa potential, then this would reinforce the generality of the Regge hypothesis.

2) Predictions of unobserved rotational transitions might be made by interpolation or extrapolation of Regge plots made with experimental data, in regions where explicit theoretical calculations are too difficult to perform.

3) Should Regge treatment be proved useful in simple molecular transitions, it could very likely be generalized to describe more complicated ones. This would provide a new theoretical constraint on experimental data. Looking very far ahead, it could develop into a non-empirical theory if the dispersion relation program is ever able to compute the appropriate trajectories.

Before closing, two features might be point out which tend to further support the credibility of this idea.

A) In the Regge formulation, after one bound state or resonance has occurred, the next must obey the selection rule $\Delta \ell = 1$, unless a new family of points has appeared. This rule must be modified (4) if there are symmetry requirements such as the Pauli principle, or exchange forces. For some nuclei the rule $\Delta \ell = 1$ is obeyed, but for even-even nuclei such an exclusion principle demands that parity be conserved, thus leading to $\Delta \ell = 2$. This seems quite analogous to the case of homonuclear diatomic molecules where only even or odd rotational states are permitted for the para and ortho nuclear spins, as compared to the

usual case where all the states are present.

B) For diatomic molecular electronic states which break up into ions as the nuclei are separated, there are an infinite number of rotational states (9). The potential at large distances is clearly Coulomb in nature, so that the Regge trajectory, as mentioned above, has an infinite number of bound states. However, for those molecular electronic states which become neutral atoms at large separations, the number of rotational states is large but finite. Could this perhaps be the expected effect for a non-Coulomb potential that the Regge trajectory must leave the real axis after a finite number of bound states? If so, it is likely (unless the trajectory loops over very quickly) that some strange type of unstable resonance, with a width much wider than the intrinsic width or rotational states, exists at the next higher value of angular momentum past the last bound state.

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